CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Anambra Basin has a total sediment thickness of about 9km, and presents an economically viable hydrocarbon Province. It is characterized by enormous lithologic heterogeneity in both lateral and vertical extension. It is derived from a range of paleoenvironmental settings ranging from Campanian to Recent (Akaegbobi, 2005). The search for commercial hydrocarbon (oil and gas) in the Anambra Basin has been on-going by oil companies and research groups. Initial efforts were unrewarding and this led to the neglect of this basin in favor of the Niger Delta Basin (Reijers, 1996; Nexant, 2003).

With the increasing global energy demand and the advent of improved technology, exploration efforts are yielding positive result in the basin. With this situation, it has become necessary to evaluate and characterize the petroleum source rocks potential of the basin, hence this study.

Maturity of organic matters is one of the most important processes in the evaluation of sources rock (Tissot and Welte, 1984). Rock-eval pyrolysis and vitrinite reflectance are the most commonly used methodsn in the assessment of the maturity of organic matter.

1.2 Statement of the Problem

Many wells have been drilled in the Anambra Basin, but unfortunately most of these wells were reportedly dry (Onuoha, 2005). Table 1.1 shows the list of wells drilled and discoveries made in Anambra Basin**.** With this situation, it has become necessary to evaluate and characterize the petroleum source rocks potential of the basin, hence this study.

Table 1.1: List of wells drilled and discoveries made in Anambra Basin (after Onuoha, 2005)

Well	Total Depth (TD) (M)	Remarks
Aiddo	3214	Dry
Ajire -1	2257	Dry
Akukwa -1	2403	Dry
Akukwa -2	3655	Gas shows
Alade -1	3055	Dry
Alo -1	2667	Gas discovery
Amansiodo -1	2291	Gas discovery
Anambra River -1	3433	Oil, gas discovery
Anambra River -2	2179	Gas shown
Anambra River -3	2430	Dry
Iguana -1	3322	Gas discovery, well was suspended
Ihanadiagu -1	2524	Gas discovery
Iji -1	3003	Dry
Nzarm -1	3672	Gas shows
Oda River -1	2400	Dry
OKPO -1	2431	Dry

1.3 Aim and Objectives

The aim of the study is to evaluate the source rocks and paleoenvironments of the Nkporo Group in the Anambra Basin.

The objectives of this study seek to;

a. Determine the organic richness of the source rocks.

b. Determine the type of organic matter and their thermal maturity

c. Evaluate the hydrocarbon generative potential of the source rocks.

d. Interprete the age and depositional environments of the source rocks of the Nkporo Group.

1.4 Scope of the Study

The scope of this study involves the evaluation of the organic geochemical organic geochemical analysis and palynological analysis of the source rocks. It covers the outcropping areas of the Nkporo Group from Abia, Nkporo, Item, Ndi-okorie, Akanu-Ohafia, Eziafor, Biakpan, Nkwebi and Leru in Abia State and Nguzu-Edda, Ebuwana and Owutu in Ebonyi State to Ugbonabo, Ogbaku, Agbogwugwu, Enugu, Emene and Ikem-Uruaram in Enugu State.

1.5 Significance of the Study

The findings of this study will be beneficial scientifically and economically.

The scientific significance of the study is that it will help the;

a. Petroleum Geologist and Geochemist to contribute to the understanding of the source rock quality and maturity of Nkporo Group

b. Palynologist to better understand the age and environment of deposition

The economic significance of the study is that if there is hydrocarbon present within the Nkporo Group, it will help in generating revenue to the country and creating employment to the people.

1.6 Location and Accessibility

The study area lies between latitudes 5° 30' N and 6° 55' N and longitudes 7° 22' E and 8° 00' E. It covers area of Abia, Ozu-Abam, Akanu, Ndi-Oji in Arochukwu Local Government Area; Ohafia, Nkporo, Item and Abiriba in Ohafia Local Government Area; Leru in Umu-Nneochi Local Government Area all the above location are in Abia State. It also covers Nguzu-Edda, Amaiyi, Ebuwana and Owutu in Afikpo South Local Government Area of Ebonyi State, Location studied in Enugu State include Ihe, Owelli, Ugbonabo in Awgu Local Government Area; Uwani and Enugu in Enugu North Local Government Area; Nike and Emene in Enugu East Local Government Area ; Ikem in Udenu Local Government Area all in Enugu State.

The study area is accessible through many roads (both major and minor roads), and footpaths. It can be accessed by the Onitsha-Enugu Express Way, Enugu- Port Harcourt Express Way, Ihe-Awgu Road, Nike – Emene Road, Item- Nkporo road, Obollo-Eke- Ikem Road etc.

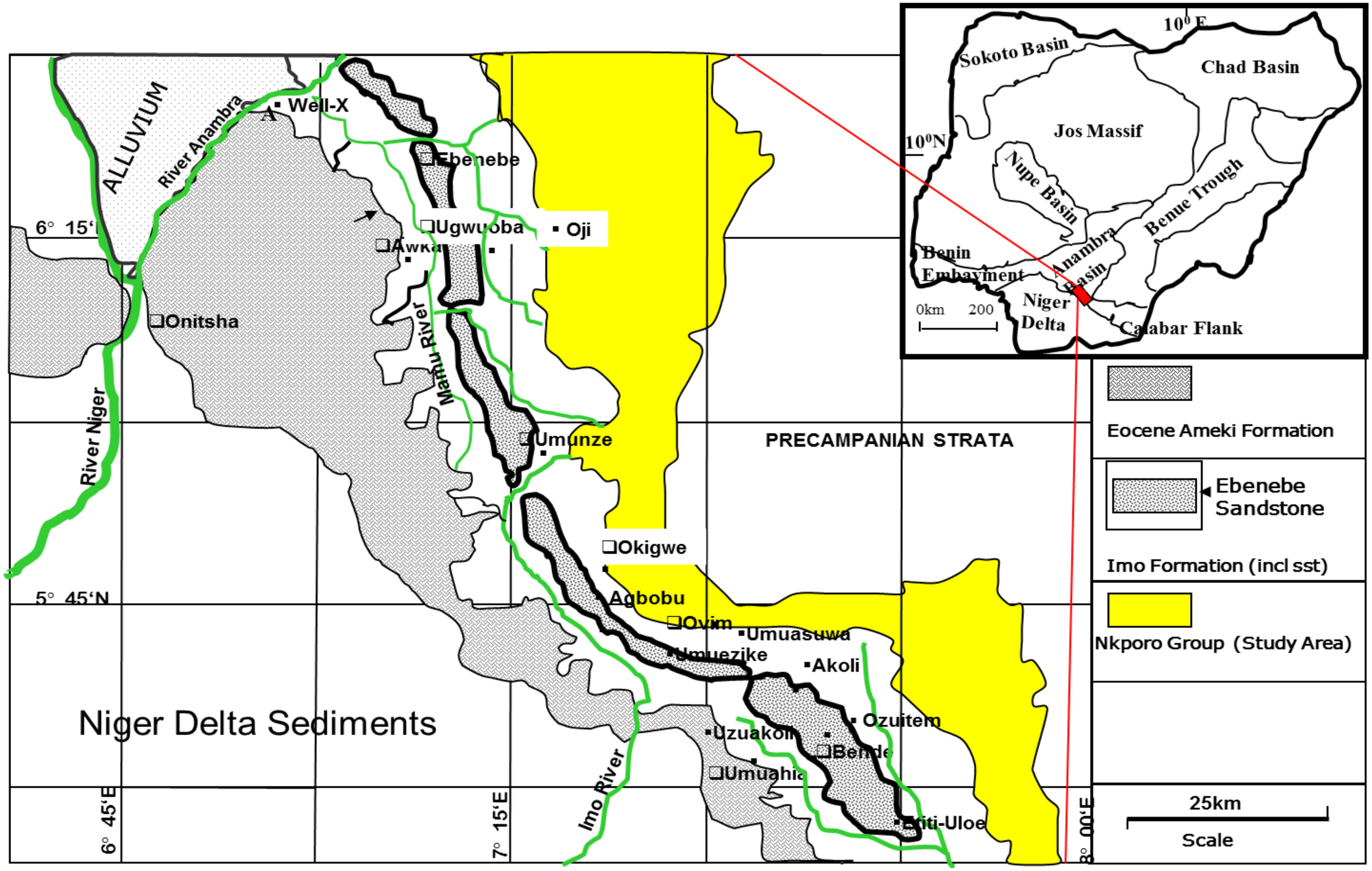

Fig. 1.1: Location Map of the Southeastern Nigeria showing the Study Area

CHAPTER TWO

LITERATURE REVIEW

2.1 Regional Geology of Anambra Basin

The Anambra Basin is a Cretaceous basin with a total sediment thickness of about 9km which can present an ideal geo-reactor for all manner of complex chemical reactions that can lead to the formation and occurrence of economically viable hydrocarbon deposits (Whiteman, 1982). The roughly triangular shaped Basin covers an area of about 40,000sq.km, located in south central part of Nigeria, and extending northwards in the Benue River (Olubayo, 2010). The basin is bounded to the south by the Niger Delta hinge line. It extends north-westward into the Niger Valley, northward to the Jos Massif and north-eastward as far as Lafia. The eastern and western limits of the basin are defined by the Abakaliki Anticlinorium and Ibadan Massif respectively. The structural evolution of the Anambra Basin has been described by Ojoh, (1992) and Obi *et al*, (2001). The origin of the basin is generally believed to be linked to the Santonian tectonics of the Abakaliki-Benue Basin, during which an N–S compression between the African and Eurasia plates folded the Abakaliki Anticlinorium (Obi *et al*, 1995). Prior to the tectonic event the Anambra Basin was a platform that was only thinly covered by sediments. The folding of the Anticlinorium laterally shifted the depositional axis into the Anambra Platform which then began to accumulate sediments shed largely from the Abakaliki Anticlinorium (Murat, 1972). The Anambra Basin-fill comprises over 2500 m of sediments that accumulated during the Campanian–Maastrichtian Period.

2.1.1 Evolution of the Anambra Basin

The Anambra Basin developed as a result of the Santonian tectonic event which greatly affected the Benue Trough terminating sedimentation in the Abakaliki Basin. Before then, sedimentation in southern Nigeria which began in the Early Cretaceous was facilitated by the breakup of the African and South American continents leading to the formation of the Benue Trough (Burke *et al*, 1970; Benkhelil, 1989). Sedimentation in the trough was controlled by three major tectonic phases, giving rise to three successive depocentres (Short and Stauble, 1967; Murat, 1972; Obi *et al*, 2001; Oboh-Ikuenobe *et al*, 2005). These three phase were

a. The Abakaliki Benue phase (Albian- Santonian)
b. The Anambra Basin phase (Campanian-Mid Eocene) and
c. The Niger Delta phase (Late Eocene-Pliocene)

The first phase (Albian–Santonian) featured the deposition of the Asu River Group, Eze-Aku and Awgu Formations within the Abakaliki-Benue Trough which was flanked to the east by the Anambra Platform and to the southwest by the Ikpe Platform (Short and Stauble, 1967; Murat, 1972; Obi *et al*, 2001; Oboh-Ikuenobe *et al*, 2005). The second phase (Campanian-Eocene) was characterized by compressive movements along the NE-SW axis which resulted in the folding and uplift of the Trough into an anticlinorium. This forced the Anambra Platform to subside and formed the Anambra Basin and the Afikpo Syncline. The deposition of the Nkporo Group, Mamu Formation, Ajali Sandstone, Nsukka Formation, Imo Formation and the Ameki Group then followed. The third sedimentary phase credited for the formation of the petroliferous Niger Delta commenced in the late Eocene as a result of a major earth movement that structurally inverted the Abakaliki region and displaced the Depositional axis further to the Anambra Basin (Obi *et al*, 2001). Reyment, (1965) undertook the first detailed study of the southern Nigeria sedimentary basin and he proposed many of the lithostratigraphic units in the region.

2.1.2 Tectonic Framework of Anambra Basin

The study area lies within the Anambra Basin. It is bounded on the eastern flank by the Abakaliki Anticlinorium and on the southwestern side by the Benin Hinge (Merki, 1972) and to the west; it separated from the Dahomey Basin by the Okitipupa Ridge. Ekine, (1989) referred to Anambra Basin as an interior fracture basin, whose origin and development is genetically related to the Benue-Abakiliki Trough. The landscape of Anambra Basin is dominated by cuesta topography, an asymmetrical ridge, with its western end at the left bank of the River Niger at Idah. It stretches to northeastern direction and, from close to the River Benue, turns southwards passing through Enugu and north of Okigwe; then swings east and terminates near Arochukwu at the right bank of the Cross-River. Its crest constitutes along sigmoidal drainage divide between the Anambra River plain to the west and the cross catchment area to the east (Fig. 2.1).

2.2 Regional Stratigraphic Setting of Anambra Basin

The oldest succession in the Anambra Basin is Nkporo Group (Nwajide, 1990). It was deposited in Late Campanian, Comprising Nkporo Shale, Owelli Sandstone and Enugu Shale (Reyment, 1965; Obi, 2000). Nkporo Group is overlain by Mamu Formation (Fig 2.2). It was deposited in early Maastrichtian (Kogbe, 1989; Obi, 2000). It comprises succession of siltstone, shale coal seam and sandstone (Kogbe, 1989) (Table 2.1). The Ajali Sandstone (Maastrichtian) overlies the Mamu Formation (Reyment 1965; Nwajide 1990), which consists mainly of unconsolidated coarse-fine grained poorly cemented sand stone and siltstone (Kogbe 1989). The Ajali Sandstone is overlain by dichronous Nsukka Formation (Maastrichtian - Danian) which is also known as upper coal measure (Obi, 2000).

Table 2.1: Characteristics of the stratigraphic components of the Campanian- Eocene Anambra Basin (modified from Avbovbo and Ayoola, 1981).

Unit	Age	Characteristics
Nsukka Formation	Maastrichtian	Tidal –estuarine sandstone, dark shale /sandy shale with thin coal seams.
Ajali Formation	Maastrichtian	Unconsolidated to poorly cemented, strongly cross bedded sandstone, siltstone and carbonateous mud rock mainly tidal deposits (Ladipo 1988).
Mamu Formation	Maastrichtian	Tidal-estuarine facies dominated by poorly consolidated carbonaceous sandstone, siltstone and mud rock with coal seams.
Nkporo Group	Campanian-Maastrichtian	Marine- Tidal flat facies comprising carbonaceous shale and mud rock with thin bed of sandstone, siltstones and Shelly limestone beds and poorly consolidated medium to coarse sandstone. Fossil – baring and inconsistent coals present.

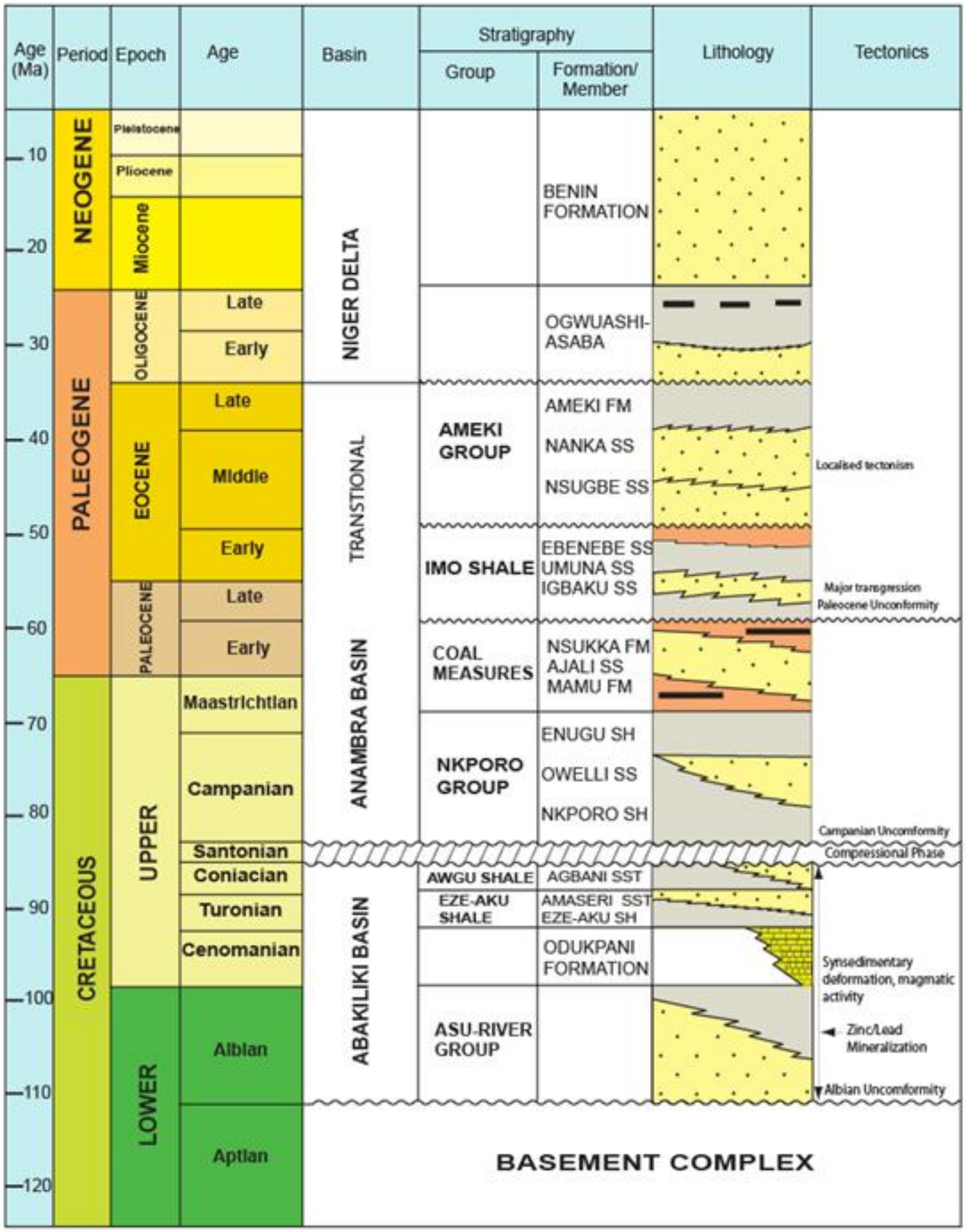

Fig. 2.1: Stratigraphic Succession in the Anambra Basin and Outcropping Niger Delta (Ekwenye and Nichols, 2016)

2.3 Review of Related Literature

2.3.1 Concepts of Organic Geochemistry

Petroleum system concept was developed through petroleum geochemistry. The ability to identify number of petroleum systems in sedimentary basin uniquely depends on geochemical techniques such as Total Organic Carbon (TOC), Rock-Eval Pyrolysis, and Paleontological Analysis. Adequate amount of organic matter is a necessary prerequisite for sediment to generate oil and gas (Akaegbobi and Schmitt, 1998). Thermal maturity provides an indication of the maximum paleotemperature reached by a source rock. The thermal maturity of the shales and coals of the Anambra Basin have been discussed by several authors (Akaegbobi and Schmitt, 1998; Akaegbobi *et al,* 2000; Unomah and Ekweozor, 1993).

The degree of thermal maturity could be assessed using pyrolysis-derived parameters such as Vitrinite Reflectance (R_o), production index (PI), Rock-Eval, T_{max} and Thermal Alteration Index (TAI). The T_{max} value, represent the temperature at which the largest amount of hydrogen is produced in the laboratory when a whole rock sample undergoes a pyrolysis treatment.

Rock-Eval pyrolysis is often performed on samples with TOC content greater than about 0.5% (Peter and Cassa, 1994). Rock Eval is generally used to determine the hydrocarbon generative potential, maturity, kerogen type and hydrogen index (HI) of a source rock.

Several authors have demonstrated the usefulness and organic petrologic methods of accessing the generative potential and characteristics of source rocks in the Anambra Basin, (Peter, 1978; Baskin, 1972; Akande *et al,* 1998a; Ojo and Akande, 2002). The deposition of organic sediments in the Benue Trough was first reported by Murat, (1972) and examined in greater details by various workers (Petters, 1982; Petters and Ekwezor, 1982 and Akaegbobi and Schmitt, 1998).

Nwachukwu, (1985) evaluated the geochemical characters of the Asata/ Nkporo Shale and said it was probably deposited under a strong anoxic (euxinic) water condition. He also applied the time temperature index of Loptain to evaluate petroleum prospects using the geothermal gradient model. He concluded that the Benue Trough contains only little oil formed after the Santonian event which occurs stratigraphically higher than gas. He reported that the organic matter was deposited under anoxic condition. All these preliminary reports confirmed the presence of abundant organic rich shales as source rocks with organic carbon ranging from 0.22 to 4.16% within the Anambra Basin (Agagu and Ekweozor, 1982). According to Petters, (1978), a possible increase in organic richness from older to younger shale could have been due to a decrease in the preponderance of planktonic foraminifera. The idea was substantiated by Agagu and Ekweozor (1982) who reported an increase in abundance of coarse terrigenious clastic particles.

Agagu and Ekweozor, (1982) pegged the threshold of intense hydrocarbon generation (TIHG) at about 1900m in the southern Anambra Basin. The threshold temperature was inferred to be 60ºC. They further ascertained that the onset of mature source facies in the southern end of the Anambra Syncline is relatively shallower than it is in the southern onshore and western offshore of the producing Niger Delta Basin. Unomah (1987) evaluated the quality of organic matter in the Cretaceous shales of the Lower Benue Trough as the basis of the reconstruction of the factors influencing organic sedimentation. He deduced that the organic matter and shales were deposited under a low rate of deposition. Specific reference to the organic richness, quality and thermal maturity in the Mamu Formation and Nkporo Shale has been reported by Unomah and Ekweozor, (1993). Akaegbobi and Schmitt, (1998); Obaje *et.al*, (1999); Akaegbobi, (2005); Ekweozor, (2006) reported that the sediments are organic rich but of immature status.

Umuomah and Ekweozor, (1993) proposed that the shale in Anambra Basin and Afikpo Syncline contain mainly terrestrial derived organic matter and essentially gas prone. They equally stated that outcrops and near surface sections of Enugu shale are immature while the lower section is overcooked. Later Akaegbobi and Schmitt, (1998) observed that the Campanian and Maastrichian Shale is a good example of mixed terrestrially marine source rock within the Anambra Basin. They recorded that the relationship between the Hydrogen Index (HI) and Oxygen Index (OI) in the said Enugu Shale and other episodes of suboxic and anoxic conditions for the deposition of Nkporo/Enugu Shale.

Obaje *et.al*, (2004) has investigated the source rock potential of various formations in the Benue Trough and Anambra Basin. They proposed the Nkporo/Enugu Shale to be the source rock for the petroleum system in the Anambra Basin having TOC values ranging from 1.5 to 4.3wt%. Mamu Formation and Nkporo/Enugu geological units and gave a detailed comparative analysis of geochemical qualities of the shaly facie of the Mamu Formations and the underlying Nkporo/Enugu Shale facies. The Nkporo/Enugu Shale presented a better evidence of organic matter preservation and petroleum potential. On the basis of available geochemical and organic petrographic data, he identified only one petroleum system (Upper Cretaceous- Lower Paleocene petroleum system which consists of type II and III gas/oil prone Kerogen. Akaegbobi and Schmitt (1998), therefore put total volume of oil generated by Nkporo Shale and the Lower Coal Measures at 7790 million bbl of oil or 5.08 x10ft of gas which is excess of the threshold value of 50million bbl, required for expulsion of oil.

Anozie *et al*, (2014) carried out research on thermal maturation of the rock of Campanian Enugu Shale in Anambra Basin, and concluded that the hydrogen index (HI) and generation potential (GP) of the shale attained values required for a quality source rock, suggesting that the shale has gas generative potential and belong to type III kerogen with few records of type IV kerogen. The degree of thermal maturation obtained from the Rock-Eval data suggests that the shale sediments are thermally immature to generate petroleum.

2.3.2 Biomarker Geochemistry

Biomarker or geochemical fossils are organic compounds found in geosphere whose structure can be unambiguously linked to their biological origin, despite the possibility of some structural alteration due to diagenetic or other processes (Brassell, 1992). Treibs, (1934) was the first to develop the biomarker concept with his pioneering work on identification of porphyrins in crude oils and suggested that these porphyrins may have originated from the chlorophyll of plants. All biomarker molecules have definitive chemical structures, which can be related directly or indirectly through a set of diagenetic alterations to biogenic precursors, and cannot be synthesized by abiogenic processes (Simoneit, 2002). The use of biomarkers as indicators of biogenic, paleoenvironmental, and geochemical processes on earth has been widely accepted (Mackenzie *et al.,* 1982; Johns, 1986; Simoneit *et al.,* 1986; Brassel, 1992; Imbus and Mckirdy, 1993; Mitterer, 1993; Simoneit, 1998). Biomarkers are widely used in petroleum geochemical studies for source rock evaluation, oil-oil or oil-source rock correlations, basin evaluation and reservoir management (Peters *et al.,* 2005). Some of the biomarkers widely used in geochemical studies are briefly described below.

2.3.2.1 Normal and branched Alkanes

N-Alkanes are widely distributed in various plants and other organisms and are probably the most exploited class of biomarkers (Philp, 1985). High proportions of long chain C27-C31 members relative to the total *n*-alkanes especially, n-C27 and n-C29 are typical of terrestrial higher plants, where they occur as main components of plant waxes i.e.leaf curticles, spores, pollens and resins (Bray and Evans, 1961; Meinschein, 1961; Kvenvolden, 1962; Eglinton and Hamilton, 1963; Miranda *et al*, 1999; Tissot and Welte, 1984; Barthlot *et al*, 1998).

The short chain *n*-alkanes with odd-to-even predominance in the medium molecular weight region (C11-C17) maximizing at n-C16 are predominantly found in algae and microorganisms (Clark and Blummer, 1967; Fowler *et al,* 1986; Miranda *et al,* 1999; Ficken *et al,* 2000).

The ratio of odd/even carbon numbered *n*-alkanes has been in use over a long period in estimating the thermal maturity of fossil fuels (Bray and Evans; 1961; Philippi, 1965; Scalan and Smith, 1970; Tissot *et al*, 1977). These ratios can be expressed as Carbon Preference Index, CPI (Bray and Evans, 1961) and improved Odd-to-Even predominance, OEP (Scalan and Smith, 1970). The CPI and OEP values above or below 1.0 indicate low thermal maturity. Values of 1.0 suggest, but do not prove, that an oil or rock extract is thermally mature. The CPI or OEP values below 1.0 are unusual and typify low maturity oils or bitumen from carbonate or hypersaline environments (Peters *et al,* 2005). Organic matter inputs do affect these ratios and therefore are mostly applied with caution.

2.3.2.2 Acyclic isoprenoids

Acyclic isoprenoids have been widely used in fossil fuel studies for characterization and correlation studies and to obtain information on depositional environment especially in lacustrine source rocks. The acyclic isoprenoids hydrocarbons; pristane, (Pr) (structure I) and phytane, (Ph) (structure II) are ubiquitous in sedimentary rocks, crude oils and coals (Bechtel *et al,* 2003). The most abundant source of pristane and phytane is the phytol side chain of chlorophyll a and b (Powell and McKirdy, 1973). In the presence of Oxygen, phytol would be oxidized to phytenic acid, yielding pristane after decarboxylation. In the absence of Oxygen, phytol would be dehydrated, yielding phytadienes, which eventually hydrogenated to phytane. The Pr/Ph ratios have been proposed as an indicator for the oxicity of the depositional environment (Powell and McKirdy, 1973; Didyk *et al*, 1978). Pristane/phytane ratio <1.0 indicates anoxic conditions during early diagenesis, and values between 1.0 and 3.0 were interpreted as reflecting sub-oxic environments (Didyk *et al,* 1978).

However, the ratio is known to be affected by differences in the precursors of acyclic isoprenoids (Volkman and Maxwell, 1986; Ten Haven *et al,* 1987). A common precursor for pristane and phytane is inferred by the similarity in their d13C values (Hayes *et al*, 1990).

High Pr/Ph (>3.0) indicates terrigenous organic matter input under oxic conditions, while low values (<0.8) typify anoxic, commonly hypersaline or carbonate source rock (Peters and Moldowan, 1993; Peters *et al.,* 2005). However, inferences from Pr/Ph ratio, particularly in the range 0.8-3.0, on the redox potential of source sediments should always be supported by other geochemical and geological data (Peters and Moldowan, 1993; Peters *et al*, 2005).

The Pr/Ph, Pr/n-C17 and Ph/n-C18 ratios are widely used as indicators of maturity and extent of biodegradation (Hunt *et al,* 2002).

Botryococcane (structure III), an irregular C_{34} isoprenoids, which originates from botryococcene is known to occur only in *Botryococcus braunii*. The green unicellular microalga *Botryococcus braunii* is widely distributed in fresh water, brackish water, saline lakes and reservoirs at temperate, tropical and arctic latitudes (Tyson, 1995). Botryococcane is a useful source- and environment –specific indicator. It is one of the most specific biomarkers used in palaeoreconstruction. Occurrence of botryococcane proves the presence of *B.braunii* in the depositional environment but lack of botryococcane does not prove that *B.braunii* was absent (Derenne *et al,* 1988).

Lycopane (structure IV), a saturated C_{40} isoprenoidal alkane has been reported to occur in various sedimentary settings deposited under fresh water, brackish marine oxic or anoxic conditions and quite a few biological precursors have been proposed (Adam *et al*, 2006). The most obvious precursor of lycopane is the C_{40} carotenoid lycopene, which occurs in numerous organisms, such as purple phototropic sulphur bacteria, and in higher plants (Peters *et al.,* 2005). An alternative source is *Botryococcus braunii* (L-strain only), which produces abundant lycopa-14 (E), 18(E) - diene (Adam *et al.,* 2006; Peters *et al.,* 2005).

Abundant lycopanes have been reported in hypersaline euxinic settings (Grice *et al,* 1998) and in mesosaline carbonates, such as the Jurassic Malm stage carbonates (Schwark *et al,* 1998). Lycopane has been proposed to be a bacterial marker derived from reduction of lycopene (Killops and Killops, 2005).

Squalene (structure V) serves as precursor to polycyclic terpenoids, steroids and carotenoids. Squalene is a major lipid produced by methanogenic, thermophillic and thermoacidophilic archaea. Abundant squalane, a saturated C30 isoprenoidal alkane, may represent a direct archaebacterial input (Matsumoto and Watanuki, 1990) or derive from diagenetic reduction of squalene, which occur in a variety of organisms. Squalane has been used as a biomarker for archaea and hypersaline depositional environments (Ten Haven and Rulkotter, 1988).

2.3.2.3 Tricyclic and tetracyclic triterpanes

Tricyclic terpanes are common in crude oils and sediments and were first observed in extract from the Green River Formation (Gallegos, 1971). The most prominent tricyclic terpanes are important components in the saturated hydrocarbon fractions of petroleum (Moldowan *et al,* 1983). C_{30} tricyclohexaprenol in bacterial membranes or malabaricatrienes from algae or bacteria could be intermediates in the biosynthetic pathway that account for tricyclic terpanes in petroleum (Peters, 2000).

Higher homologs may originate from C_{40} tricyclooctaprenol (Azevedo *et al.*, 1998) or larger precursors. High concentration of tricyclic terpanes and their aromatic analogs commonly correlate with high paleolatitude, Tasmanite-rich rocks suggesting an origin from these algal (Aquino Neto *et al.*, 1983; Azevedo *et al.*, 1992). A higher C_{19}-C_{21} tricyclic terpanes relative to C_{23} tricycloterpane can be interpreted as terrestrial organic matter (Ozcelik and Altunsoy, 2005). Tricyclic terpanes can be used to correlate crude oils and source rock extracts, predict source rock characteristics, and to evaluate the extent of thermal maturity and biodegradation (Peters and Moldowan, 1993). C_{22}/C_{21} and C_{24}/C_{23} tricyclic terpane ratios help to identify extracts and crude oils derived from carbonate source rocks while C_{26}/C_{25} tricyclic terpane ratio is useful as a supporting method to distinguish lacustrine from marine oils (Peters *et al.*, 2005).

Tetracyclic terpanes generally in the range C_{24}-C_{27} are also frequent constituents of oils and bitumens which are tentative evidence for homologs up to C35 (Killops and Killops, 2005). They are structurally related to hopanes, for which they may be formed by thermal or bacterial cleavage of the 17(21) C-C bond in the ring, although a direct bacterial source cannot be discounted (Killops and Killops, 2005; Peters *et al.*, 2005).

C_{24}-C_{27} tetracyclic terpanes are referred to as de-E-hopanes, or 17, 21-secohopanes and are more resistant to biodegradation and maturation than hopanes. Therefore they are used in the correlation of biodegraded oils (Peters and Moldowan, 1993). Abundant C_{24} tetracyclic terpane in fossil fuel indicate carbonate and evaporite source rock settings (Connan *et al*, 1986) and are also common in most marine oils generated from mudstones to carbonate source rocks. C_{25}-C_{27}

tetracyclic terpanes have also been reported in carbonate and evaporite samples (Connan *et al*, 1986).

2.3.2.4 Pentacyclic triterpanes (Non-Hopanoid triterpenoids)

Today the biological origin of most pentacyclic triterpenoids is known (Borrego *et al*, 1997). Angiosperms contain triterpenoids of b-amyrin, which on diagenesis ultimately produced the C_{30} triterpane oleanane.

The use of a-and b- amyrins as terrestrial plant markers relies on the generally accepted view that these triterpenoids are only synthesized in higher plant cells although, possibility of contaminations has been suggested (Volkman, 2003). Pentacyclic terpanes gives information on the organic matter type, maturation, and the lithology of source rocks (Waples and Machiara, 1990). Pentacyclic triterpenoids based on the oleanane, lupane and related skeletons have provided some of the most useful markers inputs of organic matter from terrestrial plants to marine sediments (Killops and Frewin, 1994; Volkman *et al*, 2000; Volkman, 2005). Oleanane frequently encountered in sediments younger than Late Cretaceous, is therefore useful as indicator of geological age (Nytoft *et al*, 2002; Ozcelik and Altunsoy, 2005).

Oleanane occurs in two isomers; 18a (H)-oleanane (structure VII) and 18b(H)- oleanane (structure VIII), the relative amount of which changes with the level of thermal maturation, and thus can be used as indicators of maturity (Ekweozor and Telnǽs, 1990). Oleanane index (oleanane/C30 hopane) can also be used to indicate the terrestrial and marine input into the organic matter (Waples and Machiara, 1990).

Gammacerane (structure IX) has been found in sediments from the Late Proterozoic, which contains some of the earliest examples of fossil protozoan (Summons *et al*, 1988) and bacteria in marine sediments (Kleemann *et al*, 1990). Its presumed precursor is tetrahymanol first isolated from the ciliate protozoan *Tetrahymena pyriformis* (Mallorry *et al,* 1963) and since then, it has been found in other eukaryotes i.e. other ciliates, ferns and fungi (Volkman, 2005). Diagenetic conversion of tetrahymanol to gammacerane most likely proceed by dehydration to form gammacer-2-ene, followed by hydrogenation or may also arise by sulphurization and subsequent cleavage of tetrahymanol (Sinninghe Damste *et.al,* 1995). High gammacerane is often seen in fresh water lacustrine sediments (Peters and Moldowan, 1993; Peters *et.al,* 2005) and in certain marine crude oils from carbonate-evaporite source rocks (Peters *et.al,* 2005). It was proposed that the gammacerane is in fact an indicator for water stratification during source deposition (Sinninghe-Damste *et al,* 1995).

Lupanes (structure X) are probably derived mainly from angiosperms, and the occurrence of these compounds should thus be expected to follow that of angiosperm group (Nytoft *et al,* 2002). Various higher plant lupanoids e.g. lupane-3b, 20, 28-triol, lup-20 (29)-en-3b, 28-diol (betulin), lup-20 (29)-en-3b-ol (lupeol), and 3b-hydroxylup-20(29)-en-28-oic acid (betulinic acid), may be possible biological precursors. Lupane occurs frequently in coals and lignites (Wang and Simoneit, 1990; Peters and Moldowan, 1993; Stefanova *et al.,* 1995) and has been identified in evaporitic sediments (Poinsot *et al.,* 1995). Lupane is reported rarely in crude oils, and this may be attributed to difficulties in its identification (Nytoft *et al.,* 2002). Lupane has similar mass spectrum and also co-elute with oleananes. Therefore lupane may be resolved partially from oleanane using gas chromatography capillary columns with polar stationary phases or via High Pressure Liquid Chromatography (Nytoft *et al.,*2002) and best quantified using GC-MS/MS methods scanning the m/z 412.4 to 369.3 transition (Peters *et al,* 2005).

2.3.2.5 Hopanoids

Hopanoids are considered biomarkers for bacteria and cyanobacteria. Most hopanes molecular fossils originate from polar constituents of prokaryotic organisms (Nytoft *et al,* 2006). The most probable biological precursor of the hopane derivatives is bacteriohopanepolyol, which are present in the cell membranes of prokaryotic organisms (bacteria and blue algae) where they played the rigidifying role by steroids in eukaryotic organisms (Ourisson *et al,* 1982; Rohmer *et al.,* 1992; Durand, 2003; Bechtel *et al,* 2007a&b). The C30 Hopanoids have also been found in some cryptogams; moss, fern (Bechtel *et al,* 2007a&b). While hopanes with 30 or few carbon atoms are often interpreted as diagenetic products of C30 hopanoids (e.g. diploptene and diplopterol), the extended hopanes have been related to C_{35} precursors, such as bacteriohopane polyols, aminopolyols and a number of composite hopanoids (Wang *et al,* 1996).

High abundance of C_{35} hopane usually found in marine carbonates and evaporitic sediments has been attributed to highly reducing depositional environments (Yangming *et al.*, 2005).

V-shape pattern of homohopane, i.e. C31>C32>C33>C34<C35 is indicative of saline lacustrine source rock deposited under anoxic, low Eh conditions (Peters and Moldowan, 1991; Yangming *et al,* 2005). Benzohopanes, which have not been reported in living organisms, are thought to be secondary transformation products of C_{35} bacteriohopanepolyol derivatives (Grice *et al,* 1998). Distribution and different ratios of hopanes are used to evaluate thermal maturity of oil and source rock. The isomerisation at C-22 can be used to assess the maturity of geological samples (22S/22S+22R). This ratio reflects the more thermally stable 22S isomer compared to the biologically derived 22R stereochemistry (Farrimond *et al,* 1998; Peters *et al,* 2005; Killops and Killops, 2005). The parameter is usually measured using the C_{31} homohopane, although the C_{32} homologues are commonly employed due to co-elution of gammacerane with C_{31} homohopane

(Farrimond *et al,* 1998). C_{27}, 18a (H)- 22,29,30-Trisnorneohopane (Ts)(structure XI) and C_{27}, 17a(H)-22,29,30- Trisnorhopane (Tm) (structure XII) ratio are used as a maturity indicator. Ts is known to exhibit a greater stability than the Tm, and with increase in maturation, Ts usually shows marked increase in apparent concentration relative to the Tm (Seifert and Moldowan, 1981). Ts/Ts+Tm ratios are not only related to maturity, but also to organic facies and depositional environments. Oils derived from carbonates usually show low Ts/Ts+Tm compared to oil generated from shales. Bitumens of anoxic and acidic hypersaline source rocks generally show high Ts/Ts+Tm (Otto *et al*, 2005).

2.3.2.6 Steroids/Steranes

Steranes are derived from sterols that are widely distributed in plants and microorganisms. The relative concentration of C_{27} and C_{29} steranes can indicate characteristics source inputs and sedimentary facies.

The predominance of C_{27} steranes in non-marine strata indicates a deep lake facies and source input of plankton (algae) while C_{29} sterane predominance shows a swamp shallow water environment and a terrestrial higher plant input (Volkman, 1986; Peters and Moldowan, 1993; Volkman *et al,* 1999; Otto *et al,* 2005; Jauro *et al,* 2007). C_{28} sterane is a unique biomarker signature of organic matter deposited in saline lacustrine facies. Sterane/hopane ratio is often used as a measure of the relative inputs of eukaryotic versus prokaryotic debris (Peters and Moldowan, 1993). Low sterane/triterpane ratio (Norgate *et al,* 1999) has been postulated to favour terrestrial paralic facies rather than peat swamp facies as organic matter source. Sterane isomerisation at C-20 has been found useful in assessing the level of thermal maturity of oil and sediments (Fig. 2.2). The 20S/20S+20R ratio (usually measured using the C29ααα steranes) is one of the most widely applied molecular maturity parameters in petroleum geochemistry

Farrimond *et al*, 1998). It is based on the relative enrichment of the 20S isomer compared with the biologically inherited 20R stereochemistry with increasing maturity. Sterane nuclear isomerisation ratio, (αββ/ αββ+ααα) is widely applied owing to its operation beyond oil window (Farrimond *et al*, 1998). In relatively immature samples, coelution of the ααα isomer with the αββ doublet is a common problem that is responsible for the relatively high αββ values at shallow depth and apparent decreases in the parameter with increasing depth (Farrimond *et al*, 1998). In highly mature source rocks, an eventual decrease in this ratio occurs (Peters *et al*, 1990).

Applications of Biomarkes in petroleum exploration

Biomarkers in an oil can reveal the;

1. Relative amount of oil-prone vs. gas-prone organic matter in the source kerogen.
2. Age of the source rock.
3. Environment of deposition as marine, lacustrine, fluvio-deltaic or hypersaline.
4. Lithology of the source rock (carbonate vs. shale)
5. Thermal maturity of the source rock during generation (Peters and Moldowan, 1993).

To characterize charge risk, these biomarker parameters can be used in a variety of innovative ways. For example, specific biomarker parameters can be calibrated against specific kerogen quality parameters in a given basin. Then, the biomarker ratios are measured in an oil sample from the basin, and the values are projected onto calibration curves to quantitatively predict characteristics of the source rock. This approach, pioneered by the founders of OilTracers, allows explorationists to assess whether oil was generated primarily from an oil-prone or gas-prone organic facies (Dahl, *et al*, 1994; McCaffrey *et al*, 1994). The information gained from oil biomarkers (source type, age, maturity, kerogen quality) when integrated into a basin model has substantial economic impact because it provides early estimates of oil quantity and GOR for exploration targets in the area of interest (McCaffrey *et al*, 1994).

2.4 Geology of the Study Area

2.4.1 Nkporo Formation

The Formation has its type locality at the Nkporo Town in Ohafia Local Government Area of Abia State. The Nkporo shale is the basal sedimentary unit that was deposited following the Santonian folding in Southeastern Nigeria and indicates a Late Campanian, based on the presence of *Afrobolivina afra* (Reyment, 1965). The formation is generally poorly exposed but has been described as coarsening upward sequence and interbed of sands and shale with occasional thin beds of limestone (Kogbe, 1974; Reyment, 1965; Whiteman, 1982; Ladipo, 1992). The Nkporo Formation encountered in the study area is subdivisible into two lithostratigraphic units, namely, a lower sandstone and an overlying carbonaceous mud rock and shale unit The basal sandstone unit is composed of ferruginized, poorly-sorted, coarse-medium grained and pebbly sandstone that rests unconformably on the tilted Coniacian- Turonian Formations. In boreholes at the proximal Alade and Nzam localities the unit is up to 150 m thick, while in the more basinal Ogbaku and Leru sections where the unit oversteps the Pre-Campanian Formations, the thickness decreases to less than 10 m.

The overlying carbonaceous mud rock unit is better developed in the more basinal area south of Awgu, where it begins with grey, bioturbated mudstone that is characterized by concretionary pyritic layers 5-10 cm in thickness. The interval passes upward into nodular, fossiliferous black carbonaceous, fissile shale inter-bedded with grey, to milky-white, sharp-based beds of limestone and very fine grained sandstone/siltstone. Limestone occurs both as nodules and thin primary bands composed largely of bivalve- and gastropod shells embedded in lime-mud. The sandstone/siltstone lenses are micaceous and wave rippled. Body fossils recovered from the interval by previous workers include ammonites represented by *Libycoceras dandense*, and *Sphenodiscus* which dominate the lower levels (Reyment, 1965; Zaborski, 1983) and pelecypod (*Inoceramus*) which occur mainly in the sandstone/ siltstone lenses at the upper levels (Arua, 1988; Okoro, 1995).

The Nkporo Formation consists of dark shales and mudstones with subordinate sandstones, oolitic ironstone and shelly limestone with commonly burrows of *Skolithos isp*, *Ophiomorpha isp.* and *Thalassinoides isp.* (Nwajide, 2013). Deposition of the sediments of the Nkporo/Enugu Formations reflects a funnel-shaped shallow marine setting that graded into channeled low-energy marshes (Nwajide, 2013). The best exposure of the Nkporo Shale is at Leru, along the Enugu – Port Harcourt express road. It is also exposed in Abia and Akanu in Arochukwu LGA; Nkporo, Item, Amaiyi in Ohafia LGA all in Abia State; Owutu, Nguzu-Edda, Ekoji and Ebunwana in Afikpo South LGA of Ebonyi State.

2.4.2 Enugu Shale

The Enugu Formation, a lateral equivalent of the Nkporo Formation, consists of grey, blue or dark shale, occasional white sandstones and striped sandy shale beds (Nwajide, 2013). The Formation has its type locality at the Enugu Municipality, with an area coverage that stretches north to Ikem- Ihandiagu area, and southwards to Awgu area (Nwajide, 2013). It underlies the Cross-River Plains east of the Enugu Cuesta and largely overlies the Awgu Shale. The formation consists mainly of shales, with two distinguishable sandstone bodies- the Otobi and the Okpaya Sandstones- which are regarded as members of the Formation (Nwajide, 2013). Most of the territory underlain by the formation is low ground except for a few laterite- capped mounds or ridges considered to be erosional resistors left behind as the Cuesta scarp retreated westwards.

Relatively consolidated siltstones and/or fine sandstones underlie some of these isolated topographic prominences (Nwajide, 2013).

A mix of native sulphur, gypsium efflorescence, shale fragments, burrows of ichnogenous Thalassinoides, growth fault have been observed in the Formation (Nwajide, 2013). The best exposure of the Enugu Shale is along the Enugu – Port Harcourt express road, Enugu- Onitsha express road and River Emene all at Enugu (Nwajide, 2013).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Desk Study

Desk study started with the review of existing literatures on work done in the study area. This includes a study of the geologic map of the study area, to find out the Formations exposed in the area. The topographic map was used to discover the major physiographic features of the area and was also used to mark out the boundaries of the area under study before the reconnaissance survey.

3.2 Field Study

Geologic field mapping was done in three different phases, which include the following:

Acquaintance/Reconnaissance study, Detailed Study and Compilation, presentation and interpretation of field data

3.2.1 Reconnaissance Study

A good desk work (study) of the relevant literatures, maps, and imageries of the field area was carried out (as part of the reconnaissance study) before the commencement of the detailed field study. A reconnaissance survey of the general study area was carried out in order to get the familiar and necessary information about the area, secure logistics and obtain the permission to carry out studies from the communities within the study area. At this stage the field crew familiarized themselves with the whole area to be mapped by noting the geographical features, rock types and structures. Notes and records of observations on field maps were taken so as to gain confidence during the detailed mapping stage. Working scheme of stratigraphic zonation of section of sedimentary strata, indices and names of all stratigraphic units were chosen.

3.2.2 Detailed Study

The reconnaissance survey was followed by a detailed geologic study/mapping. This is the stage at which field mapping operations were accomplished. At this stage, detailed observations were made. The mapping was usually started from well exposed and uncomplicated area/horizon. The detailed mapping lasted for about one week and this involved the use of the following geologic equipments:

GPS **–** used in taking the coordinates and the elevations of the locations/stations.

Compass/clinometer **–** used for taking routine dip and strike and other structural measurements and for measuring paleocurrent directions.

Field note **–** used in recording observations in the field.

Pen, pencil and eraser **–** used for writing field observations in the field.

Geologic hammer **–** used for breaking rock for the collection of samples.

Hand Auger **–** used for drilling and collecting subsurface samples

Spade **–** used in scraping off the surface samples before using the Hand Auger

Pen knife **–** used in scraping the surface of the outcrops for fresh surfaces to reveal.

Measuring Tape **–** used for measuring the thickness of beds and sedimentary structures.

Camera **–** used for taking picture of geologic features in the field during the detailed mapping.

Hand lens **–** used for magnifying features that are not macroscopic.

Topographic and geologic maps **–** show both observations (relief, outcrop/drainage features) and the geologist’s interpretation of those observations. The symbols which represent rock types and structural measurements made at individual exposures are as a matter of direct observation. The way geological boundaries and structures are inferred through unexposed ground is entirely a matter of interpretation.

Acid **–** used for testing the effervescence nature of certain rock samples, mostly for identification of carbonate rocks.

Sample bags **–** used for collection of samples.

Masking tape **-** used in labeling samples collected.

Transparent nylons **–** used for collection samples, especially friable/loose sand samples.

Marker pen **–** a water proof, quick drying ink pen used for writing numbers and names on the specimens.

Cutlass **–** used for clearing obstacles like grasses during the mapping. It is also used for security reasons.

Personal Protective Equipment (PPE) - especially appropriate clothing/outfit, sturdy shoes with traction soles, drinking water, glucose, paracetamol, etc.

One of the best methods of collecting field data of sedimentary rocks is to construct a graphic log of the section of interest (Tucker, 1981, 1982). Observation and logging of the lithologic units was the major procedure used in this detailed study. A graphic log gives a visual impression of the section. Logging of the geologic sections was done starting from the base of each section then upwards. During this process, I (the logger) moved horizontally and laterally to check for lithologic changes. Graphic logs were drawn in the field using appropriate vertical scale for the sediment thickness (usually in meters) and horizontal scale for sediment grain size. Certain features of outcrops were recorded in the field during each logging. They include: colour, bed/rock layer thickness, texture (grainsize, sorting, grain shape, and fabric), sedimentary structures, paleocurrent measurements, fossils and nature of bed contacts

The various locations/stations within the study area were identified on the base map. Contacts between lithologic units were delineated by lithology, variation in vegetation and relief. At the end of each outcrop study, samples were collected, bagged and labeled appropriately for laboratory analysis. The samples were collected for better identification of the various rock types. Enough photographs of important features in the study area were also taken during this study.

3.2.3 Compilation, Presentation and Interpretation of Field Data

This stage involves sorting of data collected during reconnaissance and detailed studies. This is the stage for the organization of geological field report. Here, the interpretation, conclusion and summary for the data gathered during the studies are drawn.

3.3 Laboratory Study

The laboratory studies (analyses and computations) done after the field mapping/studies include the following:

Geochemical Analysis, Visual Kerogen Analysis, Biomarker Analysis and Palynological analysis

3.3.1 Geochemical Analysis

Several researchers have discussed the importance of organic geochemical methods in assessing the generation potential and characteristics of source rock (Peters and Cassa, 1994; Baskin, 1997, Peters, 1986; Akande et al, 1992, Akande, 2002, Anozie et al, 2014). In order to evaluate the organic carbon content and source rock maturity different factors including organic matter richness, generating potentialities, type of organic matter and thermal maturation and expulsion potentials must be achieved. Twenty-five (25) shale samples of the Nkporo Group (Nkporo Formation and Enugu Shale) were discussed based on Hydrocarbon Analyzer with Kinetics (HAWK) pyrolysis data and Total organic carbon (Toc) (Table 4.1a and 4.1b).

3.3.1.1 Total Organic Carbon (TOC) Analysis

Twenty-five (25) shale samples were selected for the Total Organic Carbon (TOC) analysis. The Total Organic Carbon (TOC) analysis was performed by means of the LECO CS 125 carbon analyzer according to the following procedure. About 200mg of the pre-clean shale was crushed and accurately weighed into dean LECO crucibles. The rocks were de-mineralised by hot 10% HCl and afterwards washed repeatedly with distilled water. After drying at 60^0C, the crucibles were automatically introduced into the furnace for combustion and measurement of the organic carbon content.

The quantity of organic matter expressed as total organic carbon is a measure of the organic richness of sedimentary rocks (Jarvie, 1991). i.e quantity of organic matter present in rock and expressed as TOC in weight percent of the dry rock. The organic carbon richness of the rock samples (TOC %), is important in the evaluation of source rock for hydrocarbon.

3.3.1.2 HAWK Pyrolysis

An advanced pyrolysis instrument was used to identify the type and maturity of organic matter and to detect petroleum potential in sediments. This instrument is known as Hydrocarbon Analyzer with Kinetics (HAWK). HAWK pyrolysis is done using the Wildcat Technologies, HAWK™ Plus TOC module at Geomark Research, Humble, TX. U.S.A. The HAWK instrument measures all the classical pyrolysis parameters (S1, S2, S3, and Tmax) and TOC (Total Organic Carbon) using only about 100 milligrams of 60 mesh sizes ground rock sample. In addition, HAWK pyrolysis measures inorganic carbon and therefore gives you the carbonate carbon content of your rock samples. Acid preparation of samples for TOC analysis on the HAWK is not required. Utilizing the HAWK-eye software, interpretive results such as Oil Saturation, Hydrogen Index and Maturity can be obtained in near real-time to facilitate geosteering.

HAWK is ideal for analysis of not only conventional samples but also unconventional ones for which, the rock formations generative and non-generative organic carbon contents can be determined while any generated, expelled or retained hydrocarbons can be quantified. The HAWK's maximum oven temperature is 850 °C which insures complete pyrolysis of difficult to break-down Type III kerogen and also assures you that the complete decomposition of carbonates such as calcite and dolomite will occur. The HAWK also provides the capability for processing kinetics data using software such as GeoIsochem's Kinetics05. HAWK's kinetics data output can be configured to suit your needs. Whenever desired, analyses on the HAWK can continue overnight with no operator attention because it has a fully electronic, high precision autoloader with removable and interchangeable trays holding up to 126 samples. HAWK's PyroSmart panel displays real-time instrument status without the need of an external PC. All the critical parameters including gas flows are stored within the sample file so when you review your data, you can go into the data base and look into both the instrument and sample run parameters. HAWK's data file captures all real-time data associated with individual runs. In addition, HAWK can be used for designation of formation tops and geosteering while drilling. The HAWK instrument was designed with laboratory and well-site in mind. Samples chosen to be measured on the HAWK instrument are usually subsampled from the freeze-dried material previously crushed for analyses on the coulometer and CNS.

The HAWK pyrolysis method consists of a programmed temperature heating (in a pyrolysis oven) in an inert atmosphere (helium) of a small sample (~100 mg) to quantitatively and selectively determine (1) the free hydrocarbons contained in the sample and (2) the hydrocarbon- and oxygen-containing compounds (CO_2) that are volatilized during the cracking of the unextractable organic matter in the sample (kerogen). The analysis process involved the transfer of each sample into the furnace where it was heated initially at 300^0C for three minutes in an atmosphere of helium to release the free hydrocarbons (S1). Pyrolysis of the bound hydrocarbons to give the S2 peak followed immediacy as the oven temperature was ramped up rapidly to 550^0C at the rate of 25^0C/min. both the S1 and S2 hydrocarbon peaks were measured using a flame ionization detector (FID). A splitting arrangement permitted the measurement of the S3 peak (carbondioxide) by means of a thermal conductivity detector (TCD). The instrument automatically recorded the temperature corresponding to the maximum of the S2 peak. i.e. Tmax. An in-built computer processed the raw data afford the values corresponding to the respective rock-Eval indices.

In summary, the four basic parameters obtained by pyrolysis (Fig. 3.1) are as follows:

S1 = the amount of free hydrocarbons (gas and oil) in the sample (in milligrams of hydrocarbon per gram of rock). If S1 >1 mg/g, it may be indicative of an oil show. S1 normally increases with depth. Contamination of samples by drilling fluids and mud can give an abnormally high value for S1.

S2 = the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter. S2 is an indication of the quantity of hydrocarbons that the rock has the potential of producing should burial and maturation continue. This is the kerogen yield. S2 measurements are reported in milligrams hydrocarbons per gram of rock (mg HC/g rock). This parameter normally decreases with burial depths >1 km.

S3 = the amount of CO_2 (in milligrams CO_2 per gram of rock) produced during pyrolysis of kerogen. S3 is an indication of the amount of oxygen in the kerogen and is used to calculate the oxygen index (see below). Contamination of the samples should be suspected if abnormally high S3 values are obtained. High concentrations of carbonates that break down at lower temperatures than 390°C will also cause higher S3 values than expected.

Tmax = the temperature at which the maximum generation of hydrocarbons from cracking of kerogen occurs during pyrolysis. This is the temperature at the top of the S2 peak. *T*max measured in ºC and it's an indication of the stage of maturation of the organic matter.

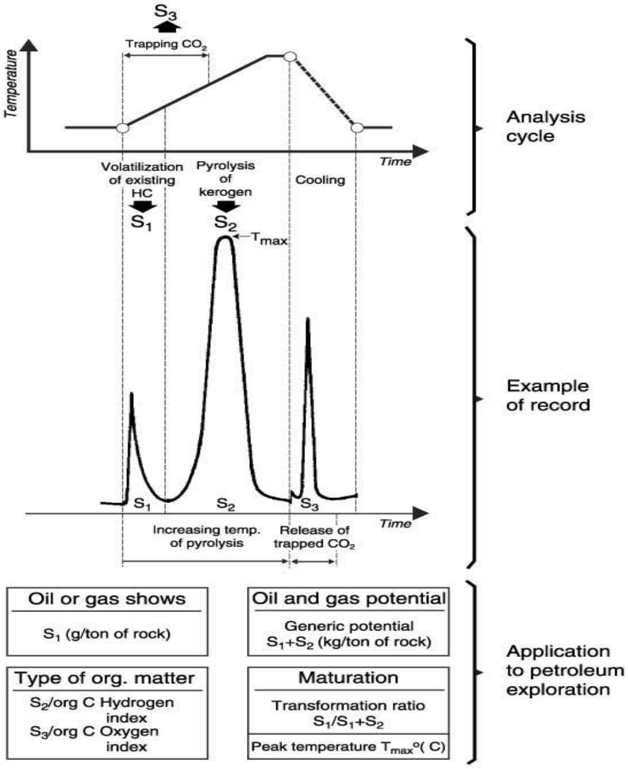

Fig. 3.1: Rock-Eval Pyrolysis Methology (Tissot and Welte, 1984)

TOC= The HAWK apparatus can also be used to determine the TOC (Total Organic Carbon) of the sample by oxidizing (in an oxidation oven kept at 600°C) the organic matter remaining in the sample after pyrolysis (residual organic carbon). The TOC is measured in weight percent (wt. %) It is determined by adding the residual organic carbon detected to the pyrolyzed organic carbon, which in turn is measured from the hydrocarbon compounds issuing from pyrolysis.

CC (Carbonate Carbon) = Measure of the inorganic carbon content of the rock and is derived from the mineral carbonate content of the rock (wt. %).

The organic richness, type, maturity, generation and expulsion potentials of organic matter in petroleum source rocks can be characterized from HAWK pyrolysis data using the following calculated parameters:

HI = Hydrogen Index (HI = [100 x S2]/TOC). HI is a parameter used to characterize the origin of organic matter. Marine organisms and algae, in general, are composed of lipid- and protein-rich organic matter, where the ratio of H to C is higher than in the carbohydrate-rich constituents of land plants. HI typically ranges from ~100 to 600 in geological samples.

OI = Oxygen Index (OI = [100 x S3]/TOC). OI is a parameter that correlates with the ratio of O to C, which is high for polysacharride-rich remains of land plants and inert organic material (residual organic matter) encountered as background in marine sediments. OI values range from near 0 to ~150.

PI = Production Index (PI = S1 / [S1 + S2]). PI is used to characterize the evolution level of the organic matter.

PC = Pyrolyzable Carbon (PC = 0.083 x [S1 + S2]). PC corresponds to carbon content of hydrocarbons volatilized and pyrolyzed during the analysis.

GP = Genetic Potential (GP = S1+ S2). GP is measured in mg/g. It can be used to evaluate the quality of prospective organic matter (Pitman et al., 1987) (Table 7).

BI= Bituminous Index (BI= [100 x S1]/TOC). BI is used to characterize the expulsion potential of the organic matter.

Calculated Ro = Vitrinite Reflectance [VR = (0.018) (Tmax) – 7.16] (Peters et al., 2005a).

Vitrinite reflectance is an optical parameter for evaluating the source rock maturity (Tissot and Welte, 1984). Vitrinite includes material derived from vascular plants (Hunt, 1996). With increasing maturity of organic matter, the reflectance (Ro) of light also increases (Peters and

Cassa, 1994). Since Tmax obtained from Rock-Eval pyrolysis indicates the level of thermal maturity, it is plausible to convert it to Ro (Dembicki Jr, 2009). This formula is applicable for type II and type III Kerogens as stated by Peters *et al.* (2005a). To obtain reasonable Ro data, the above formula was not used for samples that have S2 values smaller than 0.5 mg HC/g rock and samples with Tmax <420°C or >500°C.

Maturation of the organic matter can be estimated by (1) the location of HI and OI on Figure: (the arrows point toward increasing maturation) and (2) *T*max range. *T*max = 400°- 430°C represents immature organic matter; *T*max = 435°- 450°C represents mature or oil zone; *T*max > 450°C represents the over-mature zone. Rock Eval pyrolysis is not normally used to make real-time drilling decisions because of the lengthy sample preparation, running, and interpretation.

General Source Rock Evaluation Parameters

Peters and Cassa, (1994) described evaluation parameters of source rock (Table 3.1, 3.2, 3.3, and 3.4)

Table 3.1: Geochemical Parameters describing Quantity and Quality of Organic Matter (after Peter and Cassa, 1994)

Quantity	**TOC (wt %)**	**Rock-Eval Pyrolysis**	
		S_1	**S_2**
Poor	< 0.5	0-0.5	0-2.5
Fair	0.5-1.0	0.5-1.0	2.5-5.0
Good	1.0-2.0	1.0-2.0	5.0-10.0
Very Good	2.0-4.0	2.0-4.0	10.0-20.0
Excellent	> 4.0	>4.0	> 20.0

Table 3.2: Genetic potential value and their comparable source rock quality (Hunt 1996)

Source potential	Genetic potential value
Poor	<2 mg/g
Fair	2–5 mg/g
Good	5-10mg/g
Very Good	>10 mg/g

Table 3.3: Parameters describing Kerogen Type and the Character of Products (Peters and Cassa, 1994)

Kerogen Type	Hydrogen Index mg HC/gTOC	S_2/ S_3	Atomic H/C	Main Product at Peak Maturity
I	>600	>15	>1.5	Oil
II	300-600	10-15	1.2-1.5	Oil
II/III	200-300	5-10	1.0-1.2	Mixed Oil/Gas
III	50-200	1-5	0.7-1.0	Gas
IV	<50	< 1	< 0.7	None(Inert)

Table 3.4: Parameters describing the Level of Thermal Maturation (Peter and Cassa, 1994)

Stage of Thermal Maturity for Oil		Maturation			Generation
		R_0 (%)	Tmax (^{0}C)	TAI	PI
Immature		0.2- 0.6	< 435	1.5-2.5	< 0.10
Mature	Early	0.6- 0.65	435- 445	2.5-2.7	0.10-0.15
	Peak	0.65- 0.90	445- 450	2.7-2.9	0.15-0.25
	Late	0.9- 1.35	450- 470	2.9-3.3	> 0.25
Postmature		> 1.35	> 470	> 3.3	---

3.3.2 Visual Kerogen Analysis

In the present study, kerogen assemblages are categorized into four main groups similar to those identified by Ibrahim *et al*, (1997). These include:

Phytoclasts, refer to all structured yellow to brown colour dispersed clay- to fine sand sized particles of plant derived kerogen other than palynomorphs.

Opaques, refer to all structured brownish black to black colour oxidized or carbonized particles of plant derived kerogen.

Amorphous Organic Matter (AOM) refers to all structureless dispersed clay- to fine sand sized particles of plant derived kerogen.

Palynomorphs, refer to all structured HCl and HF resistant organic-walled microfossils. Table 3.5 shows the Batten's scale for palynomorph colours which were to observed the colours of the palynomorphs and their significance.

Procedure:

25 kerogen slides were prepared, one for each sample, for their hydrocarbon source rock potential. Each slide was examined using the transmitted light microscopy at x10, 40 and x60 magnifications in order to make a qualitative as well as a quantitative analysis of the particulate organic matter (POM), determination of the palynofacies and kerogen types, determination of spore /pollen colouration, and estimate the Thermal Alteration Index (TAI), Vitrinite Reflectance (Ro %) and organic thermal maturation. Each slide was counted for its (POM) content, in which the first 200 particles were counted in terms of *abundant* (<35 %), *frequent* (16-35 %), *common* (5-15 %) and *rare* (>5 %) (Ibrahim *et al*, 1997; Chiaghanam *et al*, 2013). Fig. 3.2 shows the Pearson's colour chart compared with organic thermal maturity, TAI and vitrinite reflectance.

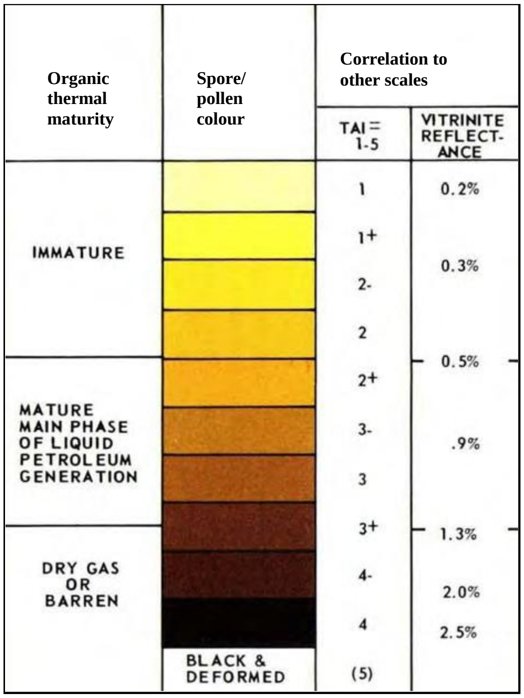

Fig. 3.2: Pearson's colour chart compared with organic thermal maturity, TAI and vitrinite reflectance (Modified from Traverse, 1994).

Table 3.5: Batten's scale for palynomorph colours (Modified from Traverse, 1994)

Observed colour of palynomorph	**Significance**
1- Colourless, pale yellow, yellowish orange.	Chemical change negligible; organic matter immature,
2- Yellow.	Some chemical change, but organic matter still immature.
3- Light brownish yellow, yellowish orange.	Some chemical change, marginally mature but not likely to have potential as a commercial source.
4- Light medium brown.	Mature, active volatilization, oil generation.
5- Dark brown.	Mature, production of wet gas and condensate, transition to dry gas phase.
6- Very dark brown-black.	Overmature; source potential for dry gas.
7- Black (opaque).	Traces of dry gas only.

3.3.3 Biomarker Analysis

The type/origin of the source rock, depositional environment/age and thermal maturity status of the organic matter contained in the samples were determined based on the distributions and abundance of aliphatic biomarkers in the shale extracts. This was achieved by using the Gas Chromatography- Mass Spectrometry (GC-MS). Ten (10) samples of the Campano-Maastrichtian Nkporo Group (Six samples from Nkporo Formation and four samples from Enugu Shale) were analyzed. These samples have high TOC, Tmax and Vitrinite Reflectance values based on the results gotten from the source rock data.

Procedures:

The saturated hydrocarbon fractions were analyzed for biomarker using a gas chromatographic system coupled with a mass spectrometer (GC-MS). Compound separation was performed on an Agilent 6890 Series GC-instrument equipped with an injection system and a fused silica capillary column (SGE BPX5; 50m length, inner diameter = 0.22 mm, film thickness = 0.25 μm). Helium was used as carrier gas, and the temperature of the GC oven was programmed from 50°C (1 min) to 310°C at a rate of 3°C/min, followed by an isothermal phase of 10 min. The injector temperature was programmed from 52°C to 300°C at a rate of 12°C/sec. For compound identification, the gas chromatographic system was linked to a Finnigan MAT 95 XL mass spectrometer operating in the electron impact mode (70 eV). Full scan mass spectra were recorded from *m/z* 50 to 650 at a scan rate of 1 s per decade and an interscan delay of 0.2 s, resulting in a scan cycle time of 1.3 s.

Table 3.6, 3.7, 3.8 and 3.9 shows oil biomarker parameters which provide information about the origin of the organic matter in the source rock, depositional environment, age and thermal maturity of the source rock respectively.

Table 3.6: Biomarker Parameters based on the type and origin of Source rock

Source Information	Biomarker Parameter	Comments
Marine Source Rock	24-*n*-propylcholestanes	Ubiquitous in oils derived from marine source rocks. (Moldowan et al., 1990)
	C42-46 Cyclopentylalkanes with odd/even carbon preference	(Carlson, *et al*, 1993; Hsieh and Philp, 2001)
Lacustrine Source Rock	Botryococcane	Presence = lacustrine source. Absence = meaningless. (e.g., Moldowan, *et al*, 1980, Metzger and Laegeau 1999)
	b-Carotane	Presence = lacustrine source. Absence = meaningless. (Hall and Douglas, 1983; Jiang and Fowler, 1986)
	Sterane/Hopanes	Low in oils derived from lacustrine source rocks. (Moldowan *et al.*, 1985)
	C26/C25 tricyclic terpanes	> 1 in many lacustrine-shale-sourced oils. (Zumberge, 1987)
	Tetracyclic Polyprenoids	High in oils from lacustrine sources. (Holba *et al.*, 2000)
	C42-46 Cyclopentylalkanes with even/odd carbon preference or with no preference	(Carlson *et al*, 1993; Hsieh and Philp, 2001)
Coal Source Rock	Pristane/phytane	Very high in coal-sourced oils; e.g., > 3.0 (Hughes *et al.*, 1995)
	C31 homohopanes	High relative to total C31-C35 in some coal-sourced oils
Higher plant input to Source Rock	Oleananes, Lupanes, Taraxeranes	Biomarkers indicating flowering plant input to source. (e.g., Ekweozor and Udo, 1988)
	Bicadinanes	Derived from Dipterocarpaceae tree resins. (Cox *et al.*, 1986)
	Retene, Cadalene	Biomarkers indicating conifer input to source. (Noble *et al.*, 1985)
	Tetracyclic diterpanes	Biomarkers indicating conifer input to source. (Noble *et al.*, 1985)
	C29 steranes	High relative to total C27-C29 steranes. (Huang and Meinschein, 1979; Moldowan *et al.*, 1985)

Table 3.7: Biomarker Parameters based on the Depositional environment and Age of the source rock

Source Information	Biomarker Parameter	Comments
Hypersaline Depositional Environment	Gammacerane	High relative to C31 hopanes in oils derived from sources deposited under hypersaline depositional conditions. High values indicate stratified water column during source deposition. (Sinninghe Damste, *et al.*, 1995)
	Pristane/phytane	Very low values (e.g., < 0.5) in oils derived from source rocks deposited under hypersaline conditions (due to contribution of phytane from halophilic bacteria). (Ten Haven *et al.*, 1987; 1988)
Anoxic Depositional Environment of Source Rock	C35 homohopanes	High relative to total hopanes in oils derived from source rocks deposited under anoxic conditions (Peters and Moldowan, 1991). Abundance of C35 homohopanes in oils (Relative to C31-C34 homohopanes) is correlated with source rock Hydrogen Index (Dahl *et al.*, 1994).
	Pristane/phytane	1.0 can indicate anoxic conditions, but the ratio is affected by many other factors.
	Isorenieratane & related compounds (2,3,6 and 2,3,4 - Trimethylaryl isoprenoids), Chlorobacteria	Presence in oil indicates anoxic photic zone during source rock deposition, since these compounds are biomarkers for green sulfur bacteria. (Summons and Powell, 1987; Grice *et al.*, 1998; Koopmans *et al.*, 1996)
	V/(V+Ni) Porphyrins	High = reducing conditions. (Lewan, 1984)
	28,30-bisnorhopane	High in certain reducing environments. (Schoell *et al.*, 1992; Moldowan *et al.*, 1984)
Age of Source Rock Deposition	Oleanane	Present in oils derived from Late Cretaceous or younger sources (Moldowan *et al.*, 1994)
	(24-norcholestanes)/(26-norcholestanes)	High in many Tertiary sources. Low values are not age-diagnostic. (Holba *et al.*, 1998A; 1998B)
	Dinosteranes, triaromatic dinosteroids	Absence always means Pre-Mesozoic, while presence USUALLY means Mesozoic or younger. (Moldowan *et al.*, 1996)
	C29 Monoaromatic Steroids	High in oils derived from sources older than 350 mybp. (Moldowan *et al.*, 1985)
	C11-C19 Paraffins	Odd-carbon-number predominance in oil from many Ordovician sources. (Douglas *et al.*, 1991; Fowler, 1992)
	(24-isopropylcholestanes)/(24-*n*-propylcholestanes)	High in oils from pre-Ordovician sources. (McCaffrey *et al.*, 1994B)

Table 3.8: Biomarker Parameter of age-related biomarkers of the source rock [(e.g Grantham and Wakefield (1988); Moldowan (2000); Moldowan *et al.*, (1994a); Moldowan *et al.*, (1996); Moldowan *et al.*, (2001a); Moldowan and Jacobson (2000); Holba *et al.*, (1998); Holba *et al.*, (2001)].

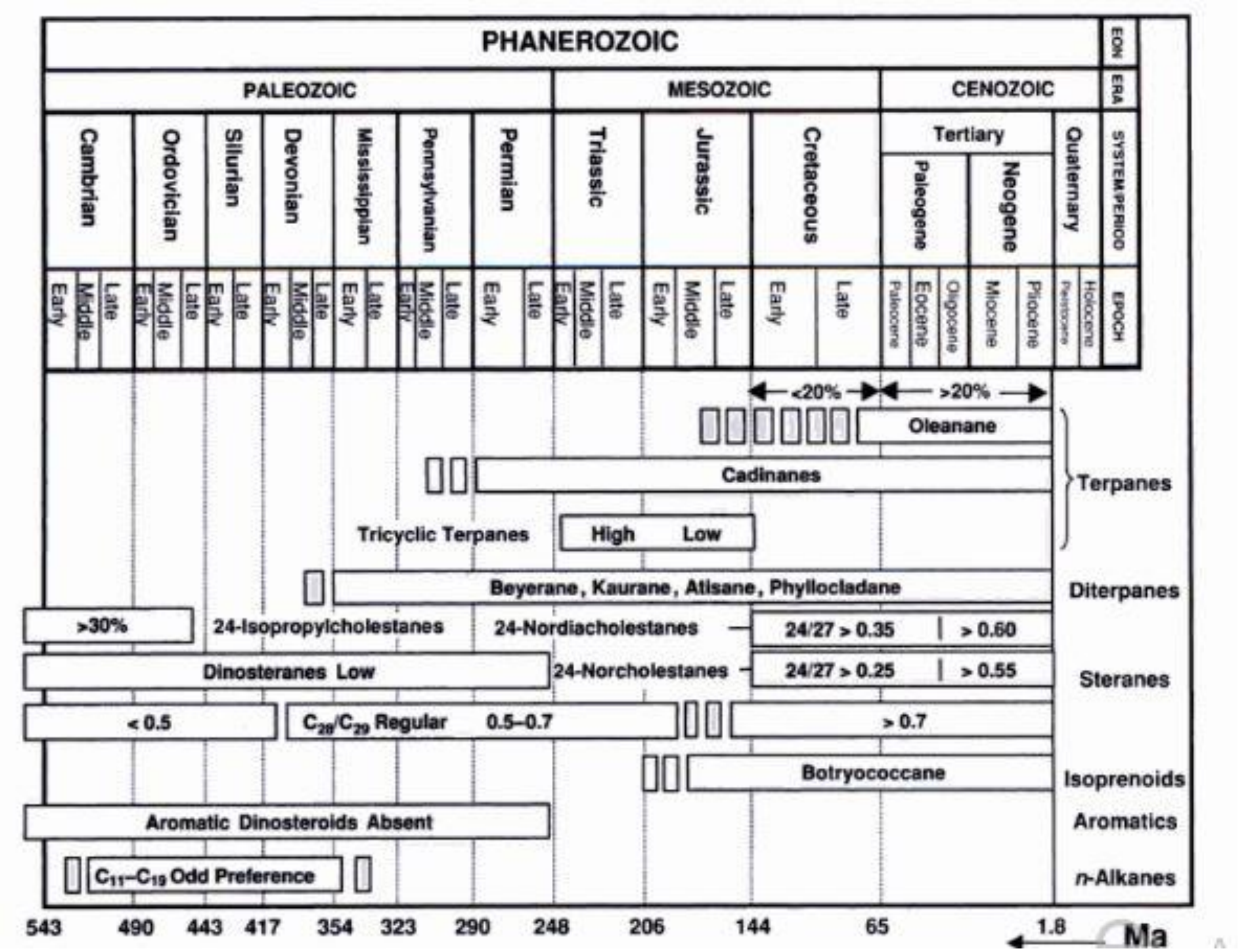

Table 3.9: Biomarker Parameters based on the maturity of the source rock

Petroleum Fractions (Compound Class)	Biomarker Parameter Measured in Petroleum Fraction	Effect of Increasing Maturity	Comments
Saturated Hydrocarbons	C29 Steranes [20S/(20S+20R)]	Increase	Useful in early to mid oil window. Decreases at very high maturity levels.
	C29 Steranes [*abb*/(*abb*+*aaa*)]	Increase	Useful in early to mid oil window.
	Moretane/Hopane	Decrease	Useful in early oil window.
	C31 Hopane [22S/(22S+22R)]	Increase	Useful in immature rocks to onset of early oil window.
	Ts/(Ts+Tm)	Increase	Also influenced by source lithology.
	Tricyclic Terpanes/Hopanes	Increase	Useful in late oil window; also increases at high levels of biodegradation.
	Diasteranes/Steranes	Increase	Useful in late oil window; also affected by source lithology (low in carbonates, high in shales); also increases at high levels of biodegradation.
Aromatic Hydrocarbons	Monoaromatic Steroids: (C21+C22)/ [C21+C22+C27+C28+C29]	Increase	Useful in early to late oil window; resistant to effects of biodegradation.
	Triaromatic Steroids: (C20+C21)/ [C20+C21+C26+C27+C28]	Increase	Useful in early to late oil window; resistant to effects of biodegradation.
	Triaromatic /(Monoaromatic + Triaromatic Steroids)	Increase	Useful in early to late oil window; resistant to effects of biodegradation.

3.3.4 Palynological Analysis

This palynological analysis is sometimes called shale analysis. Palynology studies the fossil palynomorphs – including pollen and spores – present in a rock sample. This analysis helps in determining the age of the rock. Twenty-seven shale samples got from the study area were done on this basis to determine the terrestrial species (spores and pollen) and marine species. The samples have a definite processing schedule, and thus, before any mechanical or chemical treatment, each sample was properly registered under the laboratory register book and sample number assigned. Care was taken to record data such as lithologic type, geographic location, collector's name, geologic formation, and code number. All of these data as well as processing schedules are necessary details in order to keep good permanent records of each processed sample.

The first step of the routine processing consists of crushing the material. Obviously there are samples in which crushing will not be necessary. However in consolidated rocks the surface of the sample is cut away and only its central portion is taken. This phase is usually carried out in the palynological laboratory over a steel block; in addition hammer and aluminum pie dishes are used. Generally different samples of distinct lithology are processed at the same time. Therefore, extreme care and some precautions were taken along the complete process in order to eliminate contamination and transposing of samples. Clean equipment constantly; use filtered water in the complete process; control the numbered beakers, plastic cups and the centrifuge tubes. Use of aluminum pie dishes and Styrofoam cups is also required.

As soon as the sample has been crushed it was transferred to glass beaker or Styrofoam cups where the main chemical disaggregation took place. This process is usually known as maceration. It consists mainly of the disaggregation and matrix dissolving of the sample to be processed. Generally it is carried out with corrosive acids such as HCl, HF or HNO_3. The time necessary for this treatment varies regularly from one or two hours to 24 hours or even more than two days. During this stage some sample needs to be periodically agitated. Previous moisturizing and soaking with water or having samples covered by water helps during the maceration stage. Extreme cautions were taken during this step because dangerous chemical compounds are being handled constantly. The vapors usually produced for these reagents cause not only damage to the man, they also attach optical and laboratory instruments.

Centrifugation is the part of the processing procedure that requires to be taken into account variable factor as density of the liquid, centrifuge speed, centrifugation time, size and specific gravity of the grains. Normally, running tests of different time-speed combinations are necessary when a brand new or unknown centrifuge is used. In addition, well balanced tubes during the centrifugation are required. This is obtained using approximately the same amount of liquid. The centrifugation process is carried out on complete capacity of the tube head centrifuge; when less than required samples are fummed, additional water will be used.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Outcrop Description

Location 1

Rock Types: Shale and Ironstone

Nature of Outcrop: Road cut section along Akanu-Ohafia to Abia road, after Ndi Okorie Junction

Description: Black, weathered, micaceous, fissile shale marked the base of this outcrop which has a thickness of about 5.48m (18ft). It is followed by a thin band of limestone of about 0.30m (1ft). Above the ironstone is a dark-grey to black fissile shale which is approximately 1m (3.28ft) with an overburden of about 1.22m (4ft). The total thickness of the outcrop is 8m (26.24ft) (Fig. 4.1).

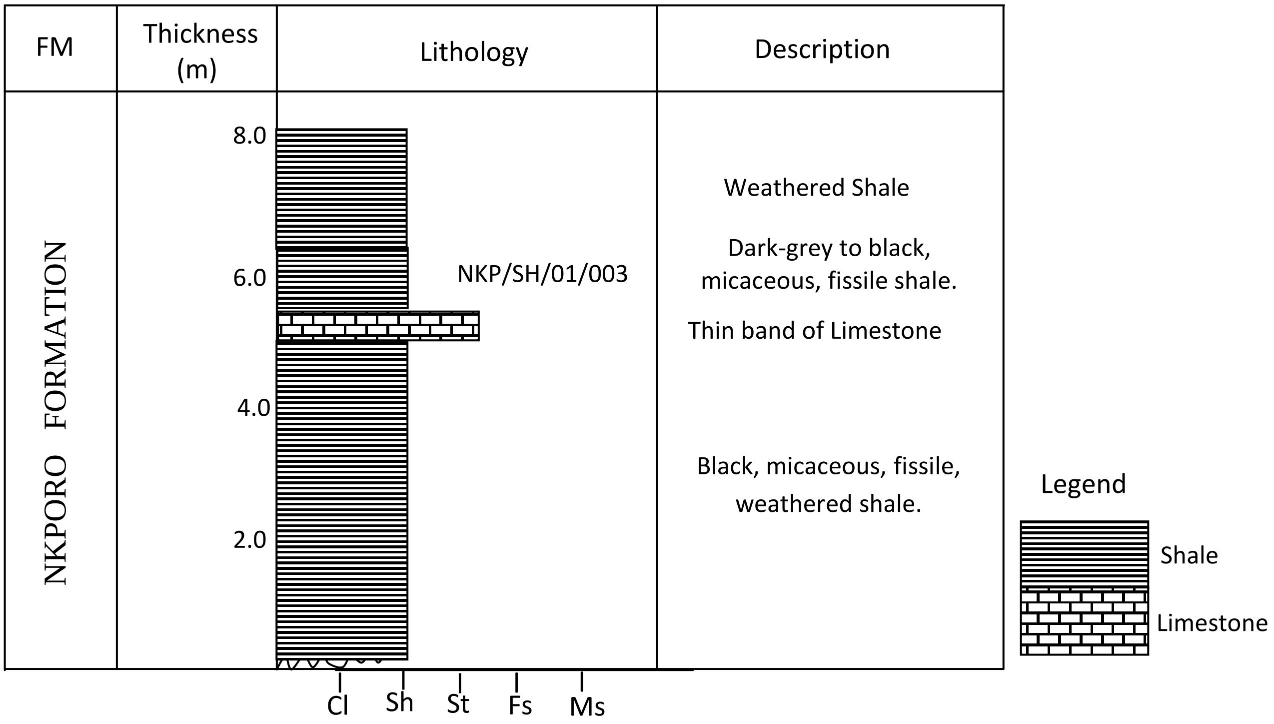

Fig. 4.1: Lithologic Section along Akanu-Ohafia to Abia road, after Ndi Okolie Junction, Abia State

Location 2

Rock Types: Shale and Sandstone

Nature of Outcrop: Oduduma Stream Section, Abia, Ohafia L.G.A

Description: The base of the outcrop is 1.22m (4ft) thick, greyish sandy clay overlained by 2.74m (9ft) of brown, poorly sorted, pebbly sandstone. The top of the outcrop is 0.61m (2ft) thick, brownish, poorly sorted, weathered pebbly sandstone. The total thickness of the outcrop is 4.57m (approx. 15ft) (Fig. 4.2a and b).

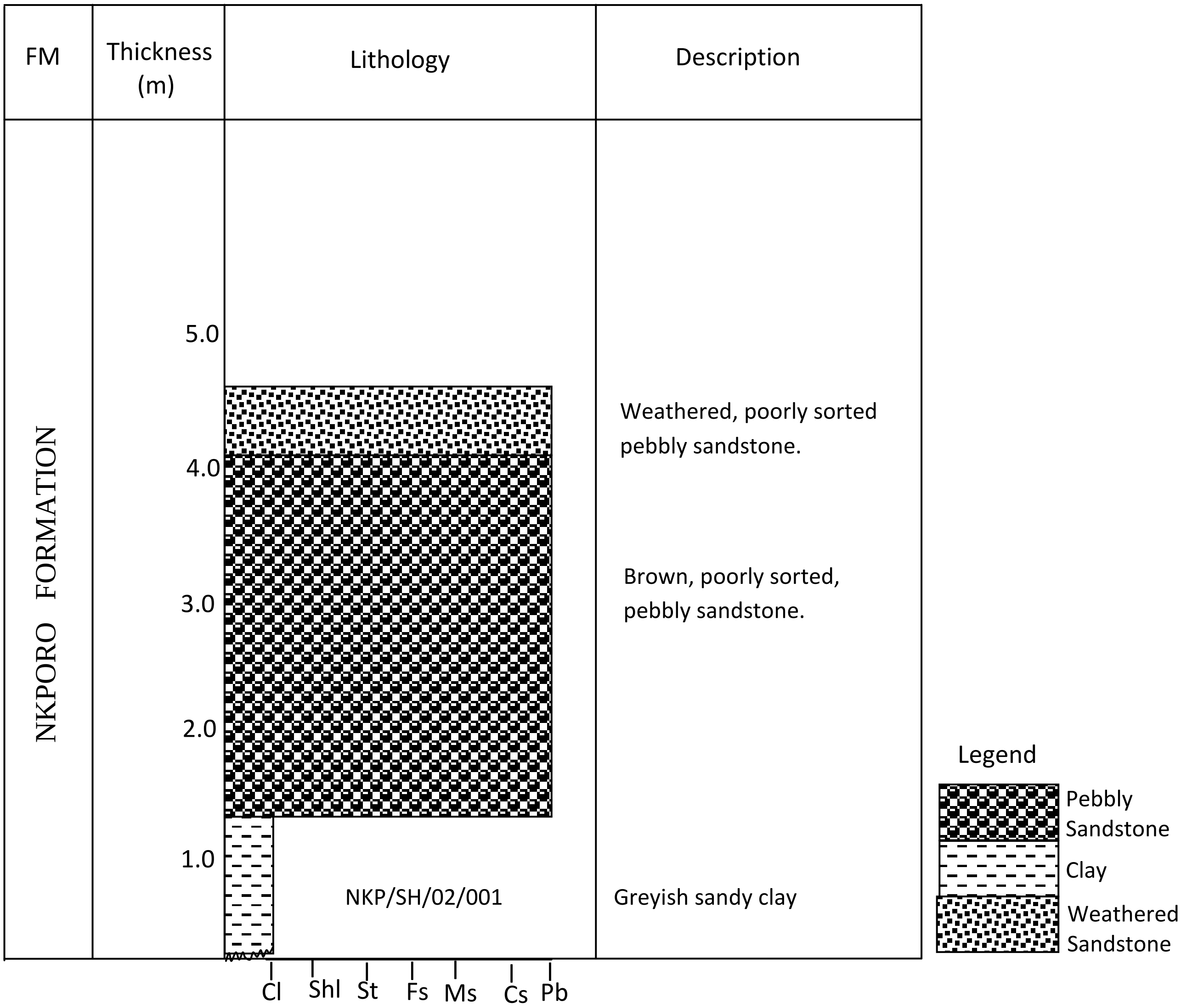

Fig. 4.2a: Lithologic Section at Oduduma stream along Ohafia-Abia Road, Abia State.

Fig. 4.2b: Photograph of the Outcrop Section at Oduduma stream along Ohafia-Abia Road, Abia State.

Location 3

Rock Types: Shale, Mudstone and Sandstone

Nature of Outcrop: Iyi-awa Spring Section, Abia

Description: Description: The base of the outcrop is 0.61m (2ft) thick of yellowish to milkish white, moderately sorted, medium grained with clay lenses. It is overlain by 1.22m (4ft) of dark-grey to black mudstone with channel sandstone unit. Between the first and second unit comes a reactivation surface with presence of trace fossils. The reactivation surface signifies a gradual break of deposition. The third unit comprise of 0.20m (approx. 0.66ft) of sandstone and mudstone intercalations. The fourth unit is about 0.15m (0.49ft) of dark-grey, fissile, carbonaceous shale which is overlain by 0.25m (0.82ft) reddish, medium grained, and moderately sorted, clayey sandstone. The sixth unit consist of 0.30m (1ft) of dark-grey to black carbonaceous mudstone which is overlain by 1.83m (6ft) of yellowish to pinkish, porly sorted clayey, pebbly sandstone. The top of the outcrop is capped by weathered, brown, medium grained sandstone, having a thickness of about 3.10 (approx. 10ft). The total thickness of the outcrop is 7.66m (25.12ft (Fig. 4.3a and b).).

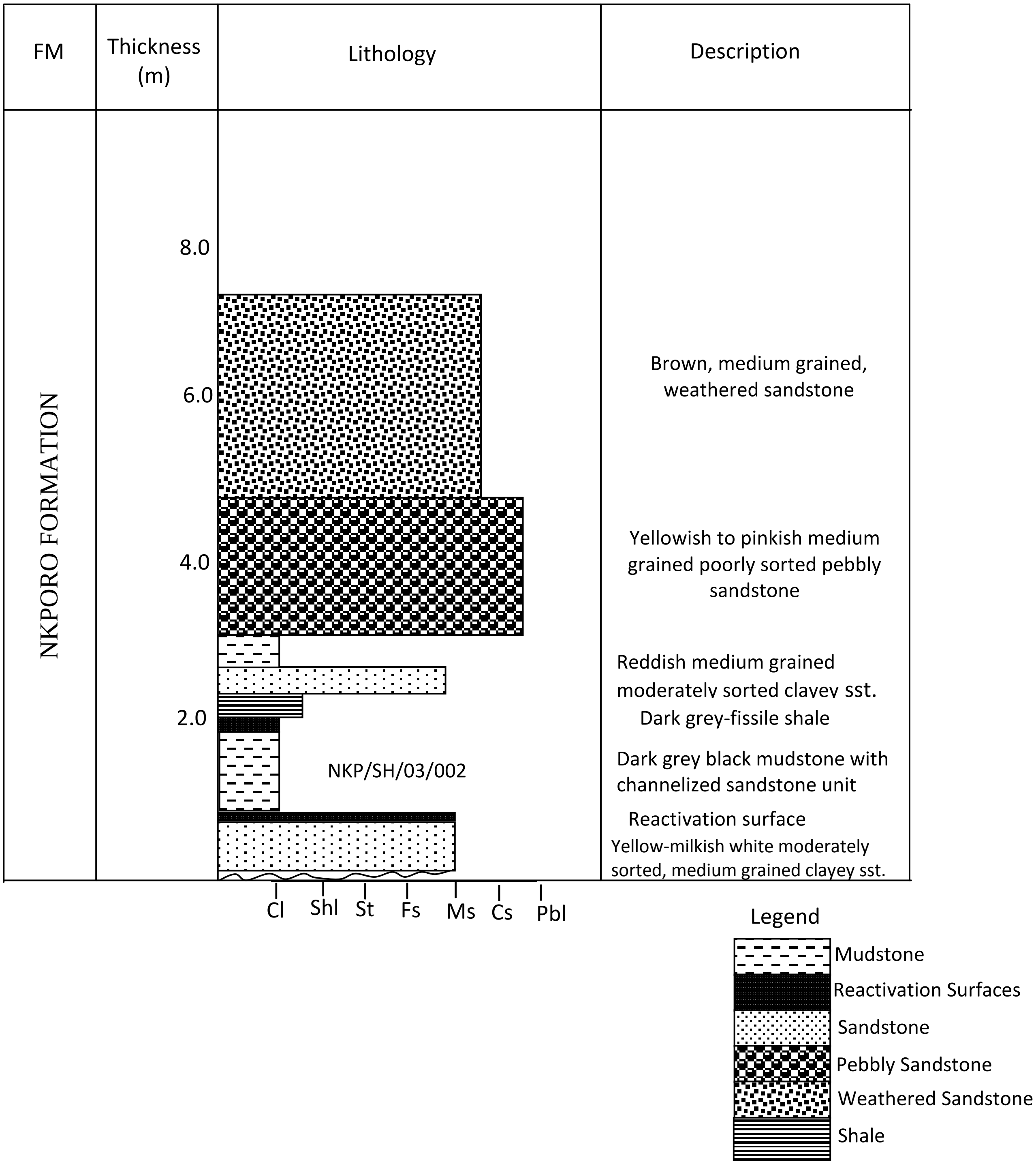

Fig. 4.3a: Lithologic Section at Inyi Awa spring section along Abia- Ohafia Road, Abia State.

Fig. 4.3b: Photograph of the Outcrop Section at Inyi Awa Spring along Abia- Ohafia Road, Abia State.

Location 4

Rock Types: Shale, Mudstone, Siltstone and Sandstone

Nature of Outcrop: Iyi-aron Spring Water Section, Abia

Description: The base of the outcrop is 2.12m (7ft) thick of grey to black, wavy laminated carbonaceous mudstone. It is overlain by 0.30m (1ft) of grey to black whitish sandy mudstone. The third unit is 0.30m (1ft) thick of grey to black carbonaceous mudstone. The fourth unit is approximately 0.5m (1.6ft) of intercalation between cemented siltstone and yellowish to white, medium grained, poorly sorted sandstone overlain by a thickness of about 1.22m (4ft) medium to coarse grained, moderately sorted, bioturbated sandstone with presence of *Ophiomopha nodusa*, *Skolithos* and *Thalasinoides*. The sixth unit is 0.52m (1.7ft) thick of yellowish, fine-grained, moderately-sorted, clayey-sandstone. This unit is consolidated with presence of bioturbation. The top of the outcrop is capped by 3.05m (10ft) thick of medium grained, moderately sorted sandstone. The total thickness of the outcrop is 8.01m (26.27ft) (Fig. 4.4a and b).

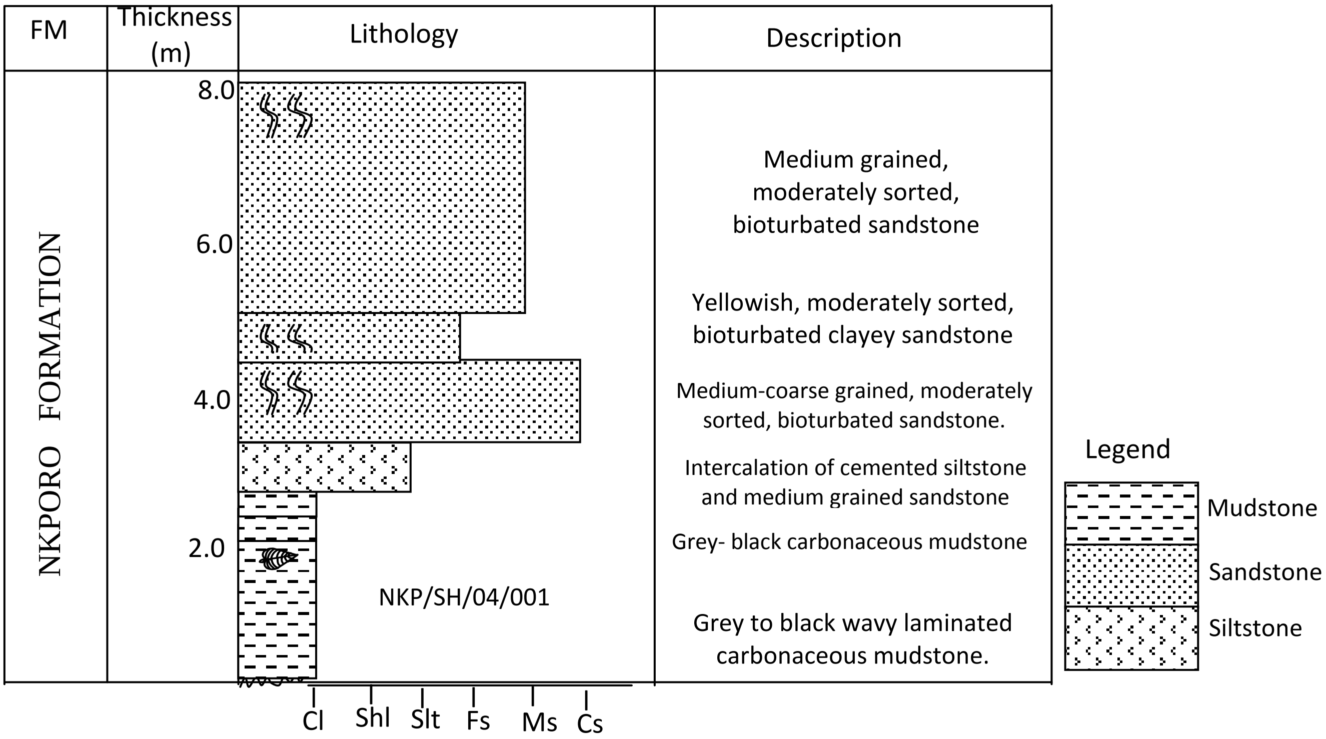

Fig. 4.4a: Lithologic Section at Inyi Aron Spring along Abia Road, Abia State.

Fig. 4.4b: Photograph of the Outcrop Section at Inyi Aron Spring along Abia- Ohafia Road, Abia State.

Location 5

Rock Types: Sandstone and Limestone

Nature of Outcrop: Ufun Stream Section, Abia

Description: The base of the outcrop is 2.13m (7ft) of medium grained, weathered sandstone. It is overlain by some limestone boulders scattered above the first unit while others were embedded inside the unit. The total thickness of the outcrop is 2.2m (7.22ft) (Fig. 4.5).

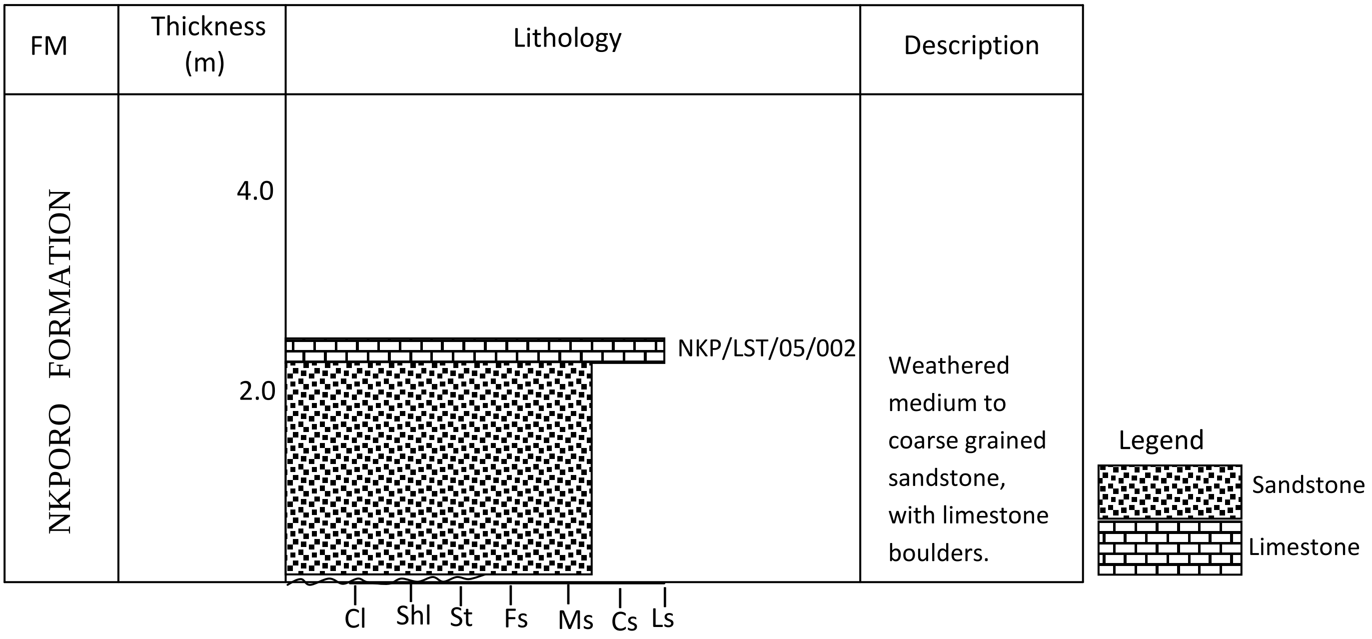

Fig. 4.5: Lithologic Section at Ufun Stream along Abia Road, Abia State.

Location 6

Rock Types: Shale, Siltstone and Sandstone

Nature of Outcrop: Road cut Section along Abia to Ukwa road.

Description: The base of the outcrop is 3.35m (11ft) thick of grey to black, carbonaceous fissile shale. It is overlain by a thin band of milk to white, carbonaceous consolidated siltstone with thickness of about 7cm (2.76inches). The third unit is 0.85m (2.8ft) thick of grey to black carbonaceous fissile shale, overlain by another thin band of whitish to dark-grey carbonaceous siltstone having a thickness of about 0.30m (1ft). The fifth unit is 0.30m (1ft) thick of grey to black fissile shale, is overlain by another thickness of about 0.32m (1.05ft) of pink to milk-white siltstone. The seventh unit is 0.73m (2.4ft) thick of grey to black carbonaceous fissile weathered shale. The top of the outcrop is capped by0.77m (2.5ft) of pinkish-white, fine-grained, moderately sorted, friable clayey sandstone. The total thickness of the outcrop is 6.69m (approx. 22ft) (Fig. 4.6).

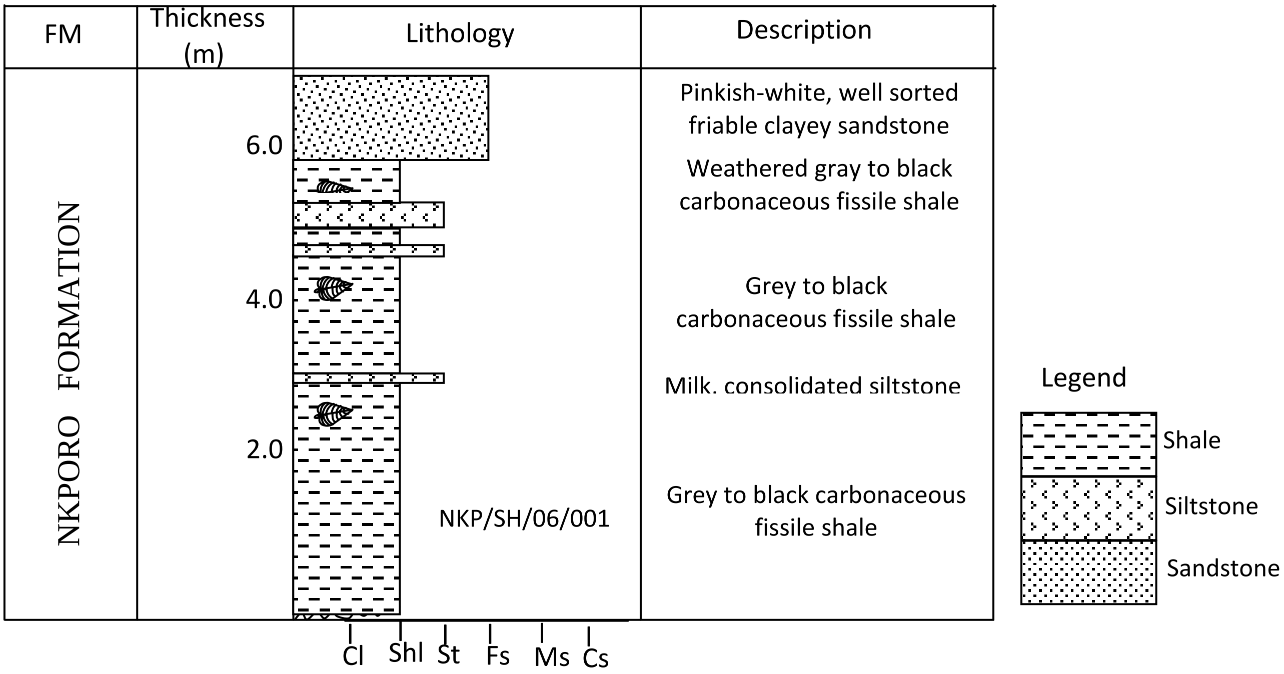

Fig. 4.6: Lithologic Section along Abia to Ukwa Road, Abia State.

Location 7

Rock Types: Shale, Siltstone and Sandstone

Nature of Outcrop: Road cut section along Eziafor to Biakpan road.

Description: The base of the outcrop is 2.44m (8ft) thick of dark grey to black, micaceous, fissile shale with very thin white/cement coloured clay lenses. It is overlain by a 0.61m (2ft) of reddish to white, coarse grained, moderately to poorly sorted, bioturbated sandstone. The third unit is 0.76m (2.5ft) thick of milk-white, parallel laminated siltstone with clay lenses. The fourth unit is 2.13m (7ft) of milk-white, coarse grained, poorly sorted sandstone, consolidated sandstone that is fractured and intensely bioturbation with presence of *Skolithos* and *Ophiomopha nodusa.* This is overlain by a reactivation surface. The fifth unit is 0.49m (1.6ft) thick of milk-white, coarse grained, poorly sorted sandstone. The sixth unit consists of 1.22m (4ft) of brown to milk-white, coarse grained, poorly sorted, semi-friable sandstone. The top of the outcrop is capped by7.62m (25ft) thick of massive, weathered brown, ferruginized sandstone. The total thickness of the outcrop is 15.27m (50.10ft) (Fig. 4.7a and b).

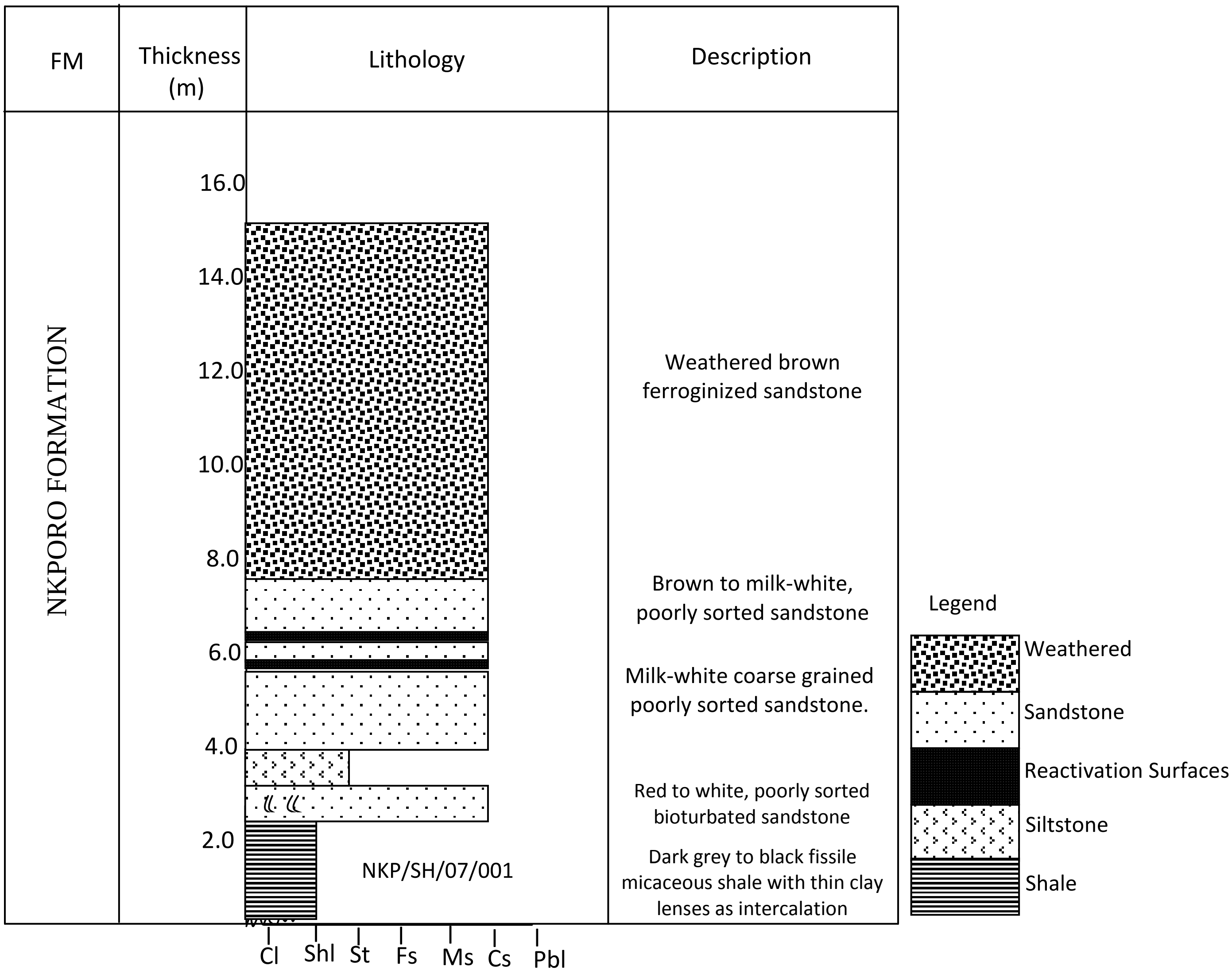

Fig. 4.7a: Lithologic Section at Eziafor to Biakpan Road, Abia State.

Fig. 4.7b: Photograph of the Outcrop Section along Eziafor to Biakpan Road, Abia State.

Location 8

Rock Types: Clay, Shale and Sandstone

Nature of Outcrop: Road cut section along Asaga-Ohafia to Eziafor road (Eziafor-Ohafia)

Description: The base of the outcrop is 4.57m (15ft) thick of dark-grey to black, carbonaceous, fissile shale. It is overlain by a reactivation surface. The second unit is 0.61m (2ft) thick of mottled weathered clay. It is overlain by another reactivation surface. The third unit comprises of intercalation of fine grained sands and clay having a thickness of about1.22m (4ft). It is followed by a reactivation surface. The fourth unit consists of 0.30m (1ft) of mottled clay, followed by a reactivation surface. The fifth unit is 0.91m (3ft) thick of white to milk clayey sandstone. It is overlain by a reactivation surface. The sixth unit is marked by white to milk, medium grained, moderately sorted sandstone which has a thickness of about 1.07m (3.5ft). It is followed by a reactivation surface. The seventh and eight units consist of white to milk, fine grained, parallel laminated sandstone, and intercalation with mottled clay having a thickness of about 0.61m (2ft). It is followed by reactivation surfaces within the units. The ninth unit comprises of white to milk clayey sandstone, fine grained, intercalation with mottled clay having a thickness of about 0.91m (3ft), which is followed by a reactivation surface. The tenth unit consists of 3.05m (10ft) of dark grey to black, micaceous, fissile shale, which is followed by a reactivation surface. The top of the outcrop is capped by weathered shale which has a thickness of about 6.10m (20ft). The total thickness of the outcrop is 19.35m (63.50ft) (4.8a and b).

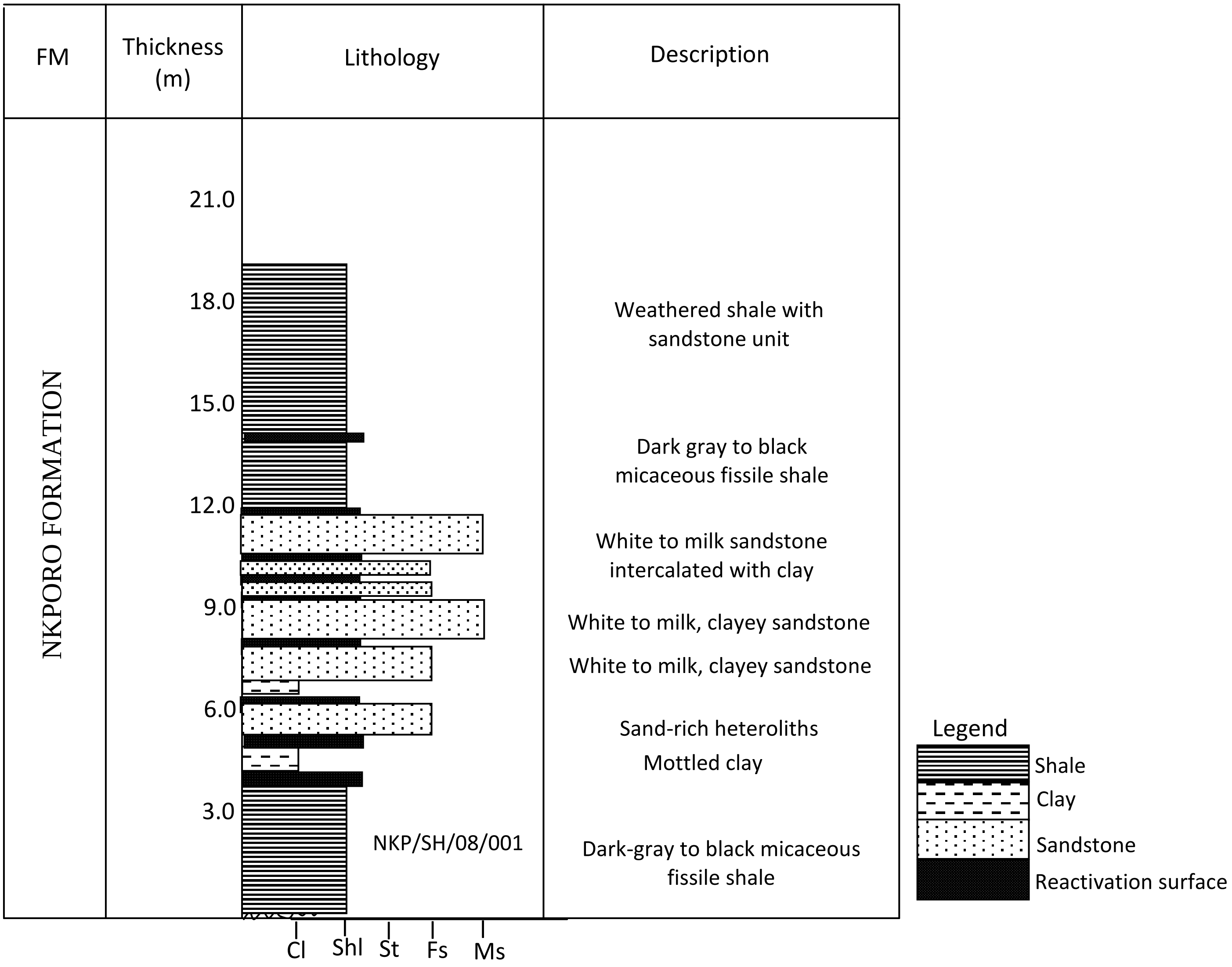

Fig. 4.8a: Lithologic Section at Asaga to Eziafor-Ohafia Road, Abia State.

Fig. 4.8b: Photograph of the Outcrop at Asaga to Eziafor-Ohafia Road, Abia State.

Location 9

Rock Types: Clay, Shale and Sandstone

Nature of Outcrop: Road cut along Okagwe-Oboro road (Nkwebi-Ohafia)

Description: The base of the outcrop is 0.30m (1ft) thick of mottled clay. The second unit consists of dark-grey to black carbonaceous shale having a thickness of about 3.05m (10ft). The top of the outcrop is capped by pinkish to brownish, fine-grained poorly laminated weathered sandstone whch has a thickeness of about 9.14m (30ft). The total thickness of the outcrop is 12.49m (approx. 41ft) (4.9a and b).

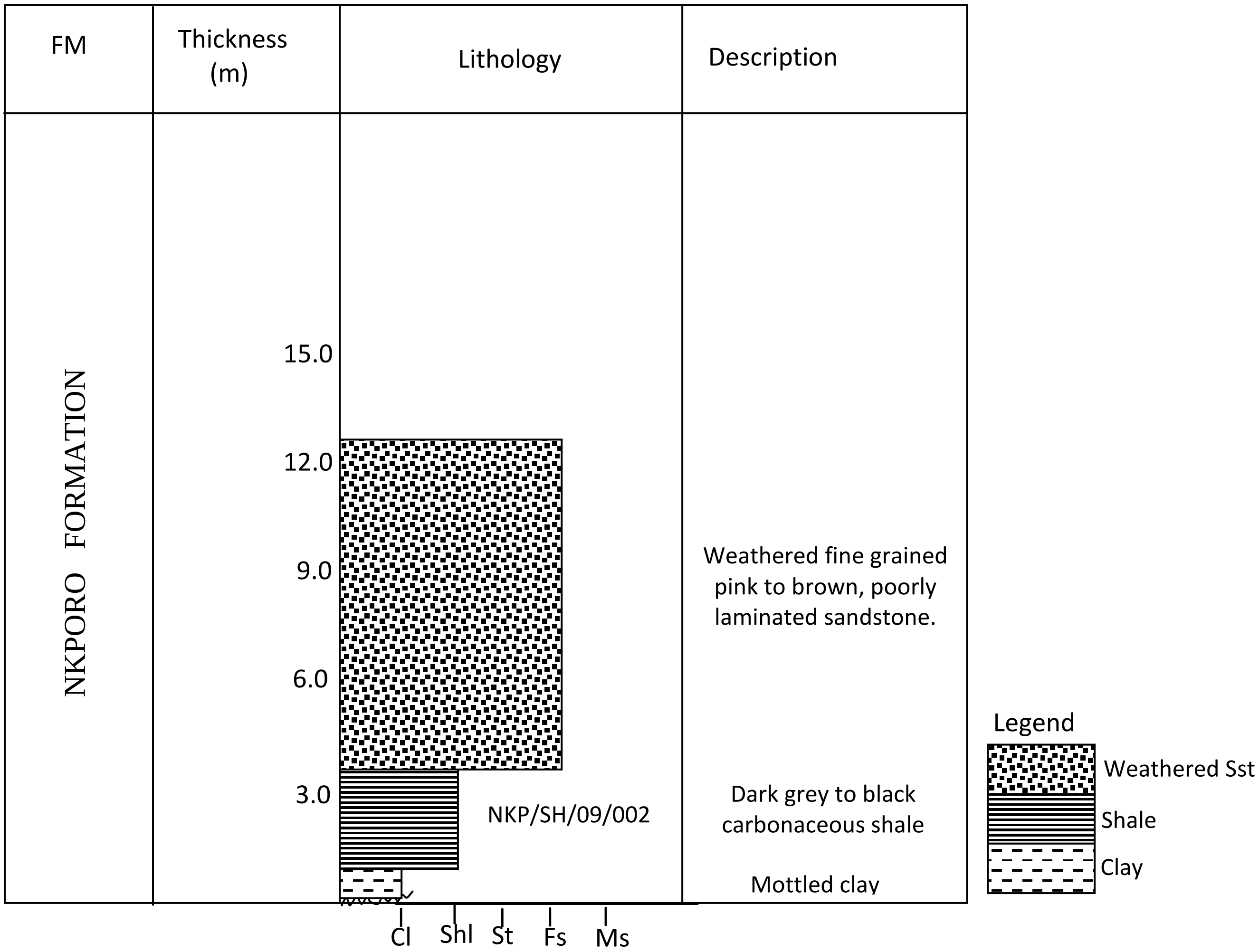

Fig. 4.9a: Lithologic Section at Okagwe-Oboro Road, Nkwebi-Ohafia, Abia State.

Fig. 4.9b: Photograph of the Outcrop Section at Okagwe-Oboro Road, Nkwebi-Ohafia, Abia State.

Location 10

Rock Types: Clay, Mudstone, Siltstone and Sandstone

Nature of Outcrop: Iyi Uruenwe Spring section, Ozu-Abam

Description: The base of the outcrop is 0.91m (3ft) thick of dark grey to mottled, mudstone. It is overlain by a reactivation surface. The second unit consists of 0.30m (1ft) of intercalation of siltstone and yellowish sandy clay. The third unit has a thickness about 1.83m (6ft) of milk-yellowish white, loose,friable, bioturbated, fine grained, well sorted, poorly laminated, clayey sandstone. The fourth unit is 0.91m (3ft) of reddish-brown sandy clay. This is overlain by a fifth unit of sandy, mottled clay of about 0.61m (2ft). The sixth unit has a thickness of about 0.30m (1ft) of consolidated, cemented, moderately sorted, bioturbated sandstone. The seventh unit consists of 4.57m (15ft) of mottled clay. This is overlain by an eighth unit of 4.88m (16ft) of reddish brown, pebbly, poorly sorted, bioturbated sandstone. The ninth unit consists of reddish to brown, fine grained, well sorted, bioturbted with presence of Skolithos and *Ophiomopha* nodusa having a thickness of about 3.66m (12ft). The top of the outcrop is 6.10m (20ft) thick capped by massive, reddish-brown, weathered, lateritic, sandy clay overburden. The total thickness of the outcrop is 24.07m (78.95ft) (Fig. 4.10 a and b).

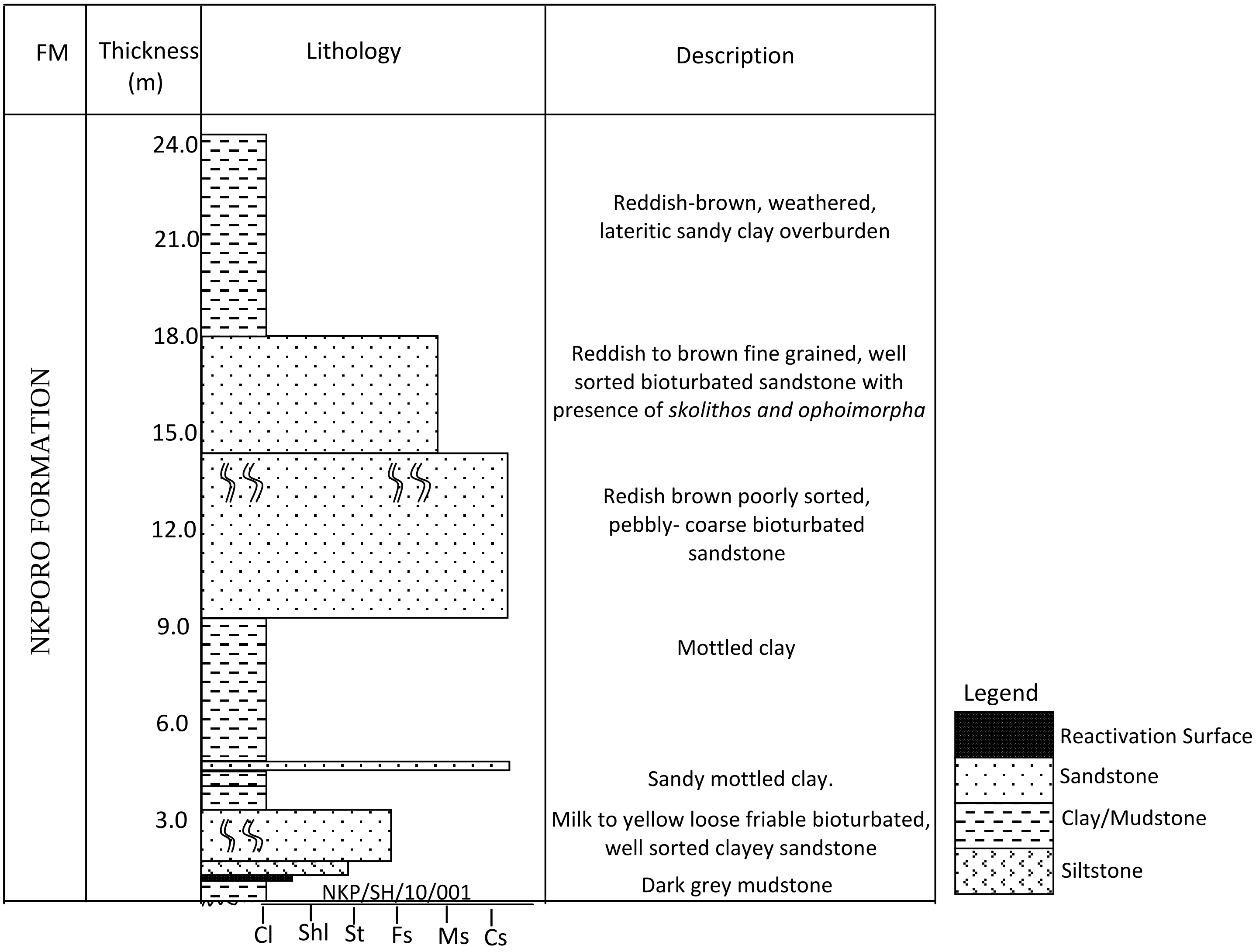

Fig. 4.10a: Lithologic Section at Iyi-Urenwe Spring at Ozu-Abam, Abia State.

Fig. 4.10b: Photograph of the Outcrop Section at Iyi-Urenwe Spring at Ozu-Abam, Abia State.

Location 11

Rock Types: Shale, Clay, Siltstone and Sandstone

Nature of Outcrop: Road cut section along Nkporo-Etiti Ama, Nkporo road

Description: The base of the outcrop is grey, fissile shale which have a thickness of about 1.22m (4ft). It is followed by a second unit of about 1.40m (4.6ft) of grey, parallel to wavy laminated, fissile shale. The third unit has a thickness of about 2.13m (7ft) of weathered mottled clay. It is followed by a thin clay unit of about 0.10m (0.33ft).The fifth unit is about 0.30m (1ft) of light brown to white medium grained, moderately sorted sandstone. It is followed by a thin clay unit of about 0.10m (0.33ft). The seventh unit consists of 1.22m (4ft) of light brown; fine grained well sorted, parallel laminated sandstone with clay lenses. It is followed by 0.55m (1.8ft) of mottled clay. The top of the outcrop is capped by weathered, ferruginized, consolidated sandstone interbedded with weathered clay, having a thickness of about 3.05m (10ft). The total thickness of the outcrop is 10.07m (33.03ft) (Fig. 4.11a and b).

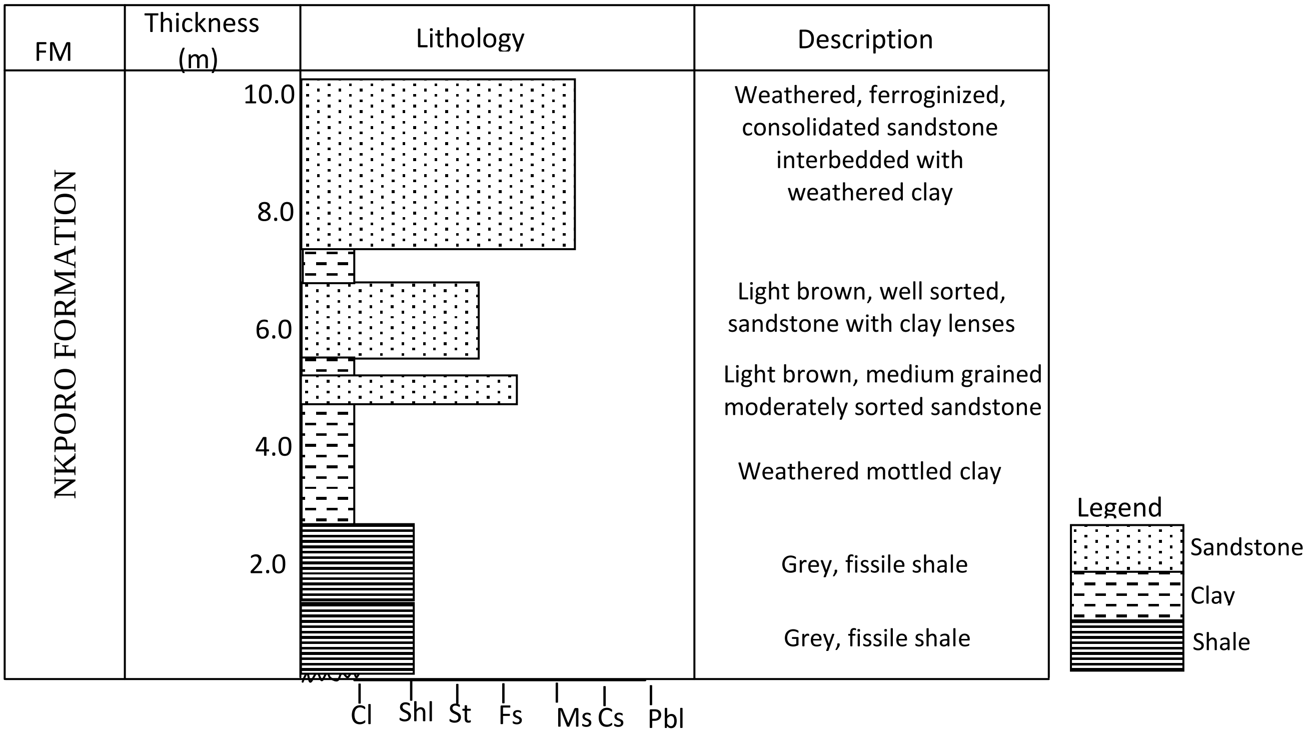

Fig. 4.11a: Lithologic Section at Nkporo-Etiti Ama Road, Abia State.

Fig. 4.11b: Photograph of the Outcrop Section at Nkporo-Etiti Ama Road, Abia State.

Location 12

Rock Types: Shale, Siltstone and Ironstone

Nature of Outcrop: Road cut section along Nguzu Owutu road (Nguzu-Edda)

Description: The base of the outcrop comprises of dark grey to black, parallel to wavy laminated, micaceous, fissile shale intercalated with siltstone which have a thickness of about 9.15m (30ft). There are presence of nodules, concretions and bivalve imprints. It is followed by 0.91m (3ft) of ironstone. The third unit has a thickness of about 6.10m (20ft) silt-rich heterolithic layer. The fourth unit is 0.61m (2ft) of ironstone, followed by a massive bed of about 5.49m (18ft) of weathered, silt-rich heterolith. The sixth unit has a thickness of about 0.76m (2.5ft) of ironstone. The top of the outcrop is capped by massive, weathered, mottled clay-rich heterolithic layer having a thickness of about 7.62m (25ft). The total thickness of the outcrop is 30.64m (100.50ft) (Fig. 4.12a and b).

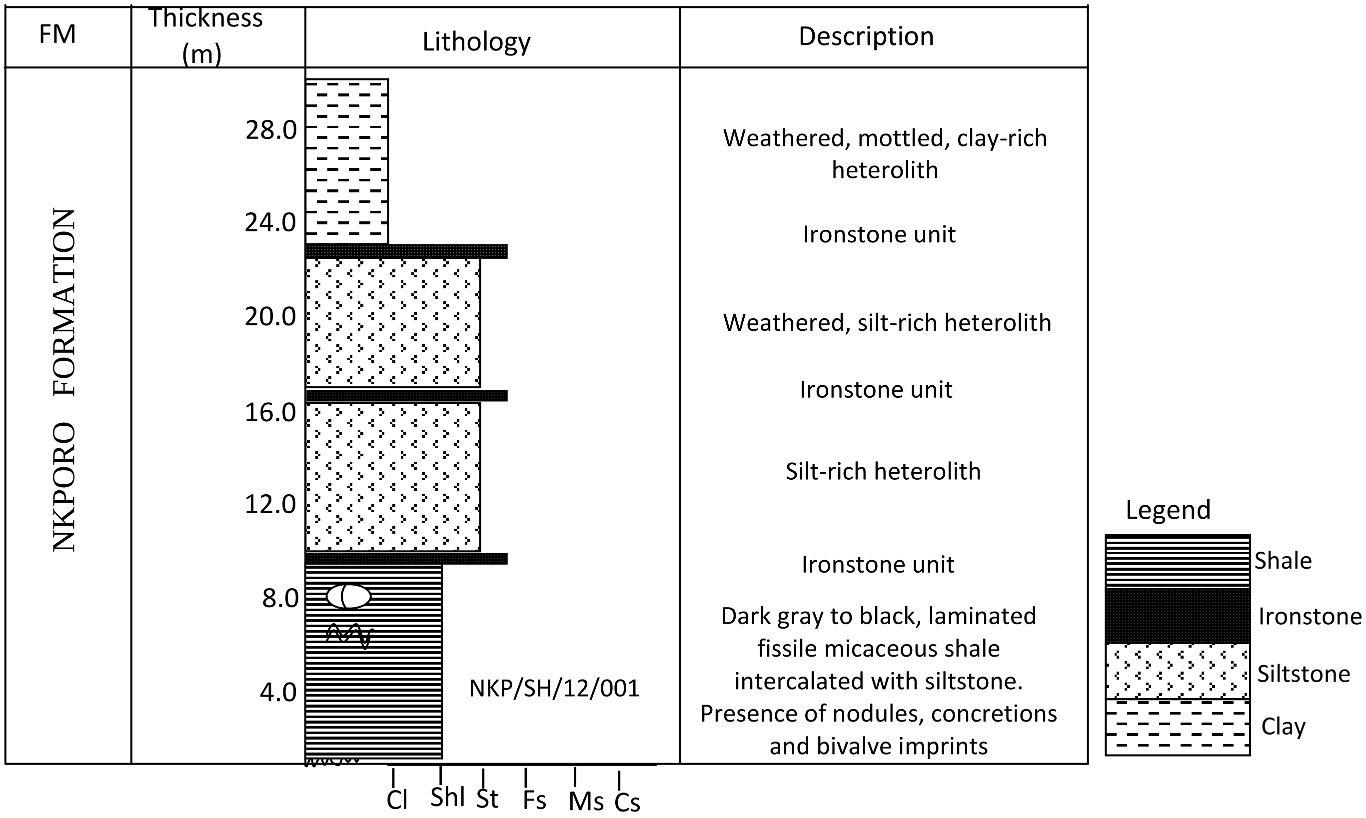

Fig. 4.12a: Lithologic Section along Nguzu to Owutu Road, Nguzu-Edda, Ebonyi State.

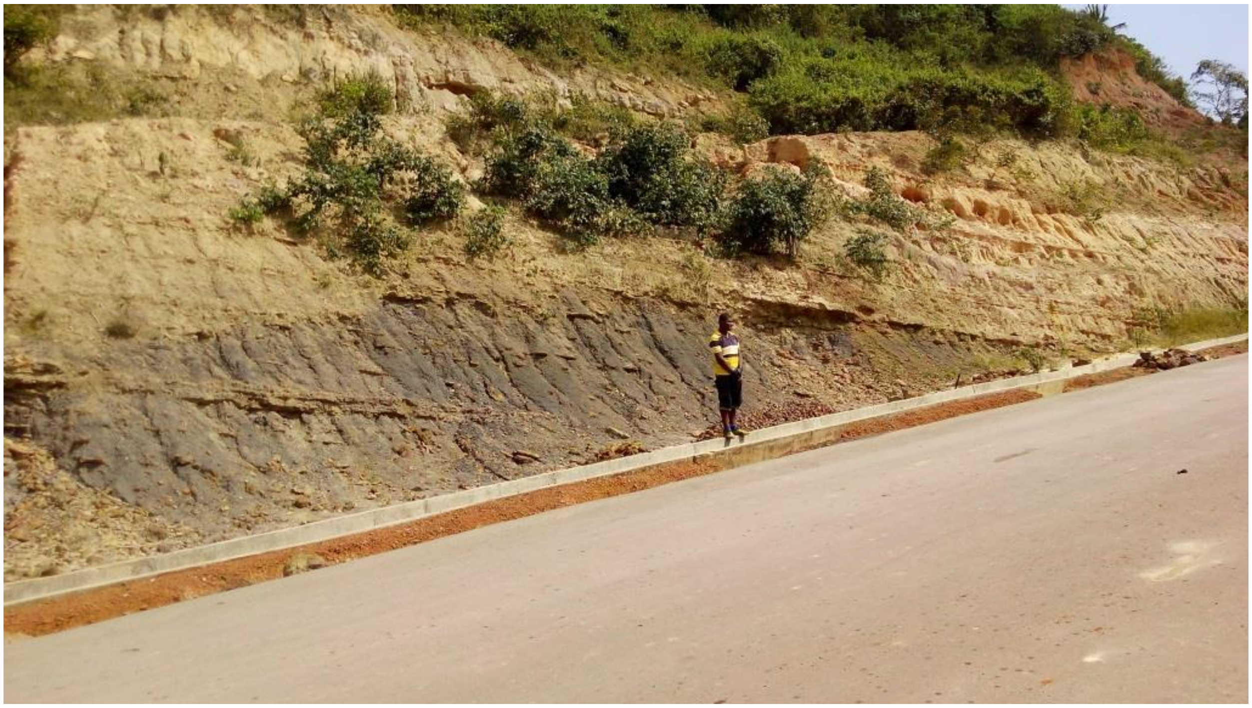

Fig. 4.12b: Photograph of the Outcrop Section along Nguzu to Owutu Road, Nguzu-Edda, Ebonyi State.

Location 13

Rock Types: Clay, Shale and Sandstone

Nature of Outcrop: Osuwowo Stream Section, Elughu-Nkporo

Description: The base of the outcrop is marked by dark grey to black, carbonaceous, wavy to horizontal lamination, fissile shale which has a thickness of about 1.86m (6.1ft). The second unit consists of mottled clay having a thickness of about 0.80m (2.6ft). The third unit comprises of light brown, weathered, fine grained sandstone having a thickness of about 2.13m (7ft). The top of the outcrop is capped by light brown to ash, poorly sorted, pebbly sandstone which has a thickness of about 1.22m (4ft). The total thickness of the outcrop is 6.01m (19.71ft) (Fig. 4.13a and b).

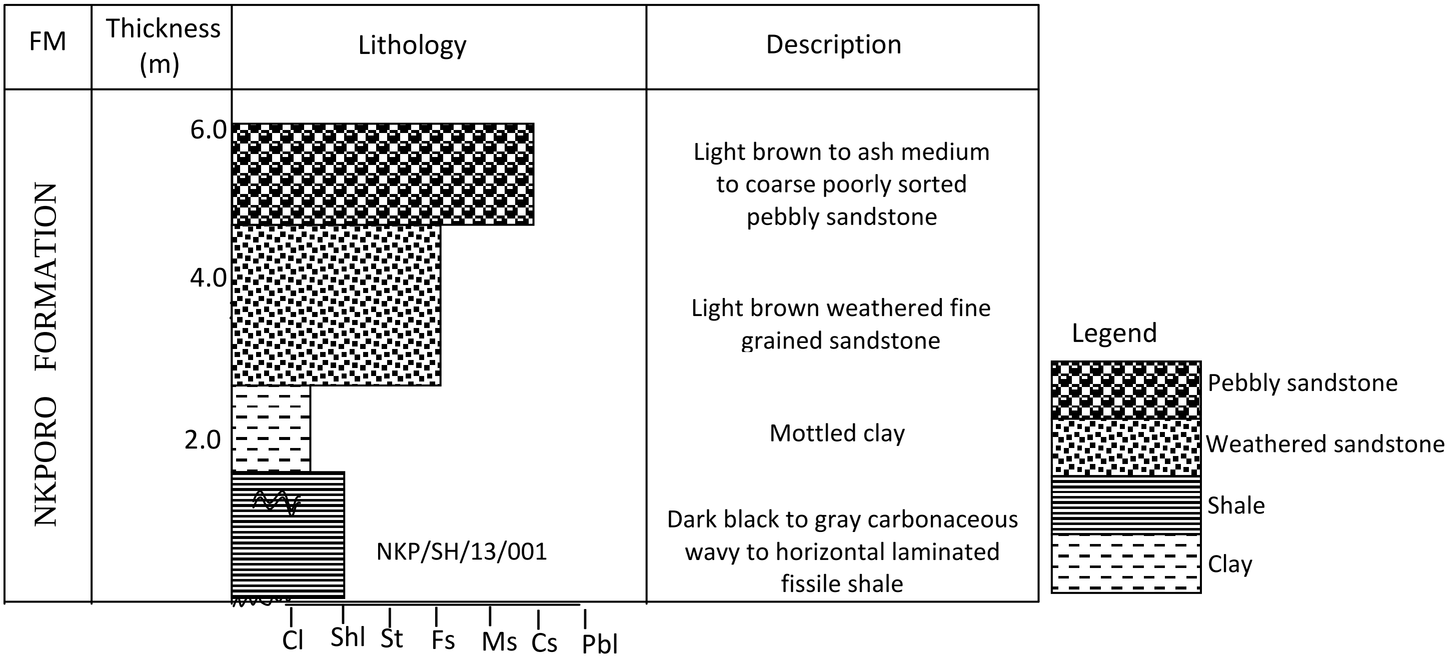

Fig. 4.13a: Lithologic Section at Osuwowo Stream, Elughu-Nkporo, Abia State.

Fig. 4.13b: Photograph of the Outcrop Section at Osuwowo Stream, Elughu-Nkporo, Abia State.

Location 14

Rock Types: Clay, Shale and Sandstone

Nature of Outcrop: Road cut section of Iyi-uzo spring along Amaokwe elu to Item road

Description: The base of the outcrop is marked by dark grey to black, carbonaceous fissile shale which has a thickness of about 1.22m (4ft). The second unit consists of mottled clay having a thickness of about 0.85m (2.8ft). The top of the outcrop is capped by light brown, fine grained, moderately sorted sandstone with presence of bioturbation which has a thickness of about 5.50m (1.8ft). The total thickness of the outcrop is 7.57m (24.83ft) (Fig. 4.14a and b).

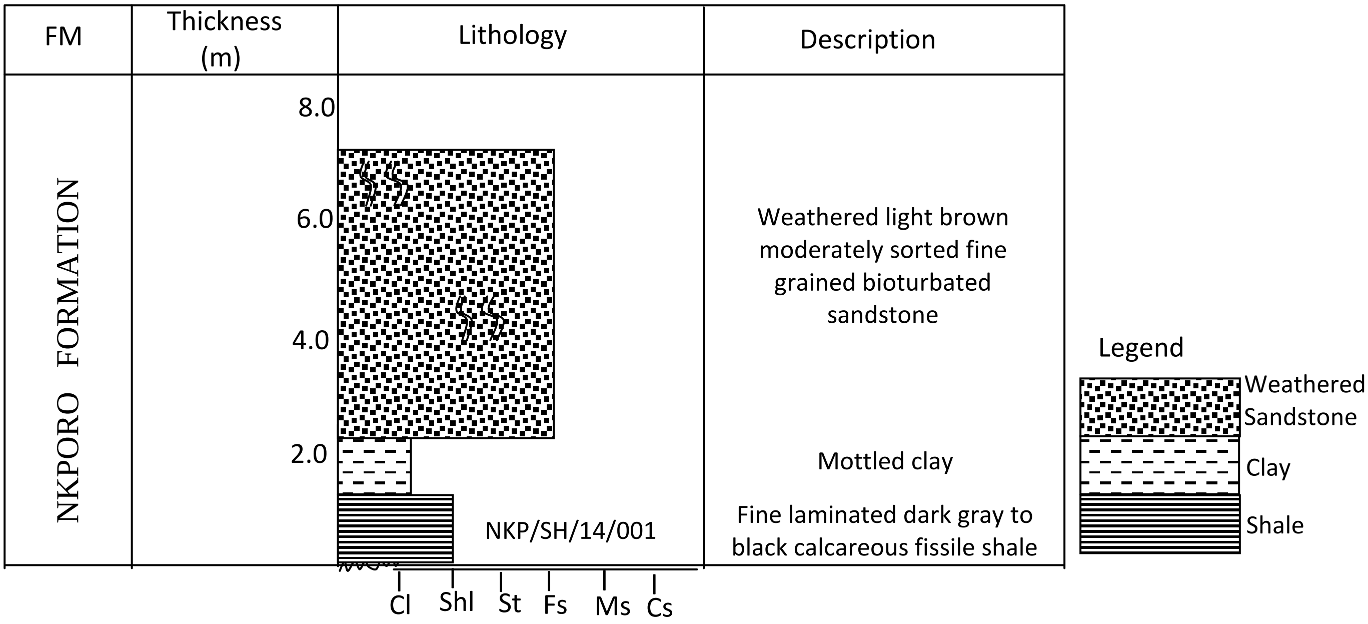

Fig. 4.14a: Lithologic Section at Iyi Uzo Spring along Okwe-elu to Item Road, Abia State.

Fig. 4.14b: Photograph of the Outcrop Section at Iyi Uzo Spring along Okwe-Elu to Item Road, Abia State.

Location 15

Rock Types: Clay, Shale and Sandstone

Nature of Outcrop: Road cut section along Asaga Amangwu Edda Community

Description: The base of the outcrop is marked by dark grey to black, fissile shale which has a thickness of about 2.5m (8.2ft). The second unit consists of mottled clay having a thickness of about 1.22m (4ft). The top of the outcrop is capped by light brown, medium grained, moderately to poorly sorted sandstone which has a thickness of about 1m (3.28ft). The total thickness of the outcrop is 4.72m (15.48ft) (Fig. 4.15).

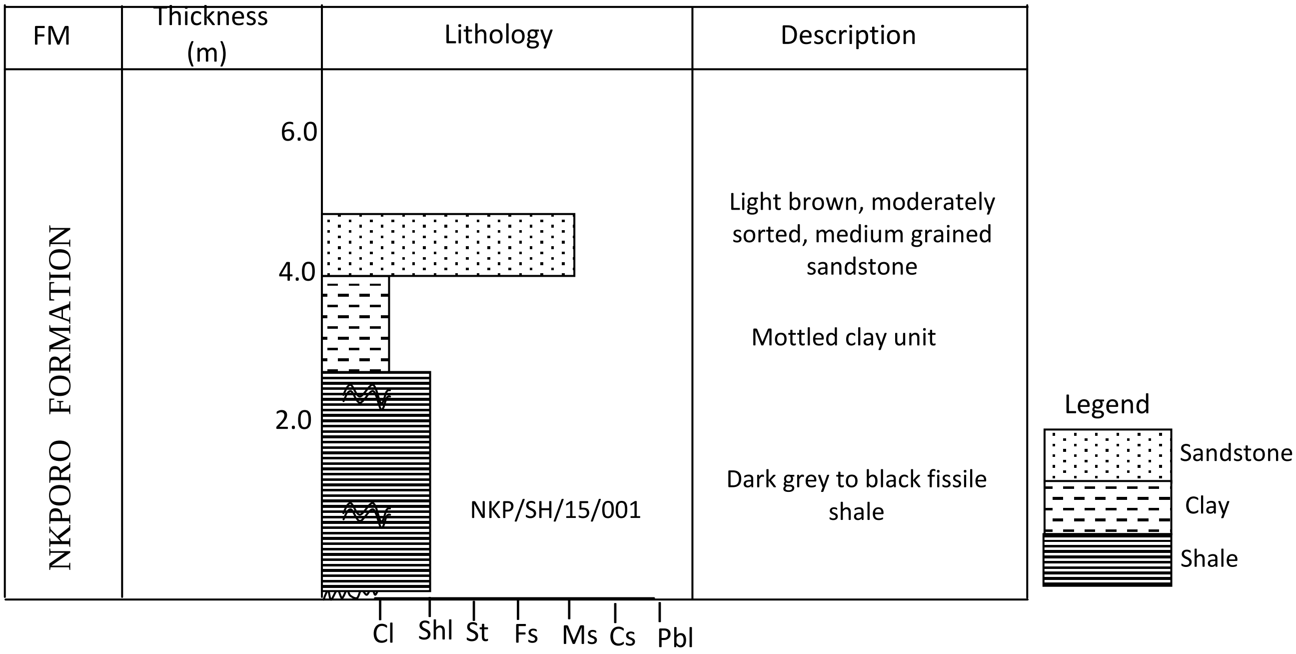

Fig. 4.15: Lithologic Section at Asaga Amangwu Edda, Ebonyi State.

Location 16

Rock Types: Shale, Ironstone, Sandstone and Limestone

Nature of Outcrop: Ochi Stream Section to the road cut section along Enugu- Port Harcourt Exp. Way, Leru.

Description: The base of the outcrop is dark grey to black, micaceous, fissile shale with very thin white/cement coloured clay lenses which have a thickness of about 2.44m (8ft). It is followed by a 0.61m (2ft) of reddish to white, coarse grained, moderately to poorly sorted, bioturbated sandstone. The third unit has a thickness about 0.76m (2.5ft) of milk-white, parallel laminated siltstone with clay lenses. The fourth unit is 2.13m (7ft) of milk-white, coarse grained, poorly sorted sandstone, consolidated sandstone that is fractured and intensely bioturbation with presence of *Skolithos* and *Ophiomopha nodusa.* This is followed by a reactivation surface. The fifth unit has a thickness of about 0.49m (1.6ft) of milk-white, coarse grained, poorly sorted sandstone. The sixth unit consists of 1.22m (4ft) of brown to milk-white, coarse grained, poorly sorted, semi-friable sandstone. The top of the outcrop is capped by massive, weathered brown, ferruginized sandstone, having a thickness of about 7.62m (25ft). The total thickness of the outcrop is 15.27m (50.10ft) (Fig. 4.16a and b).

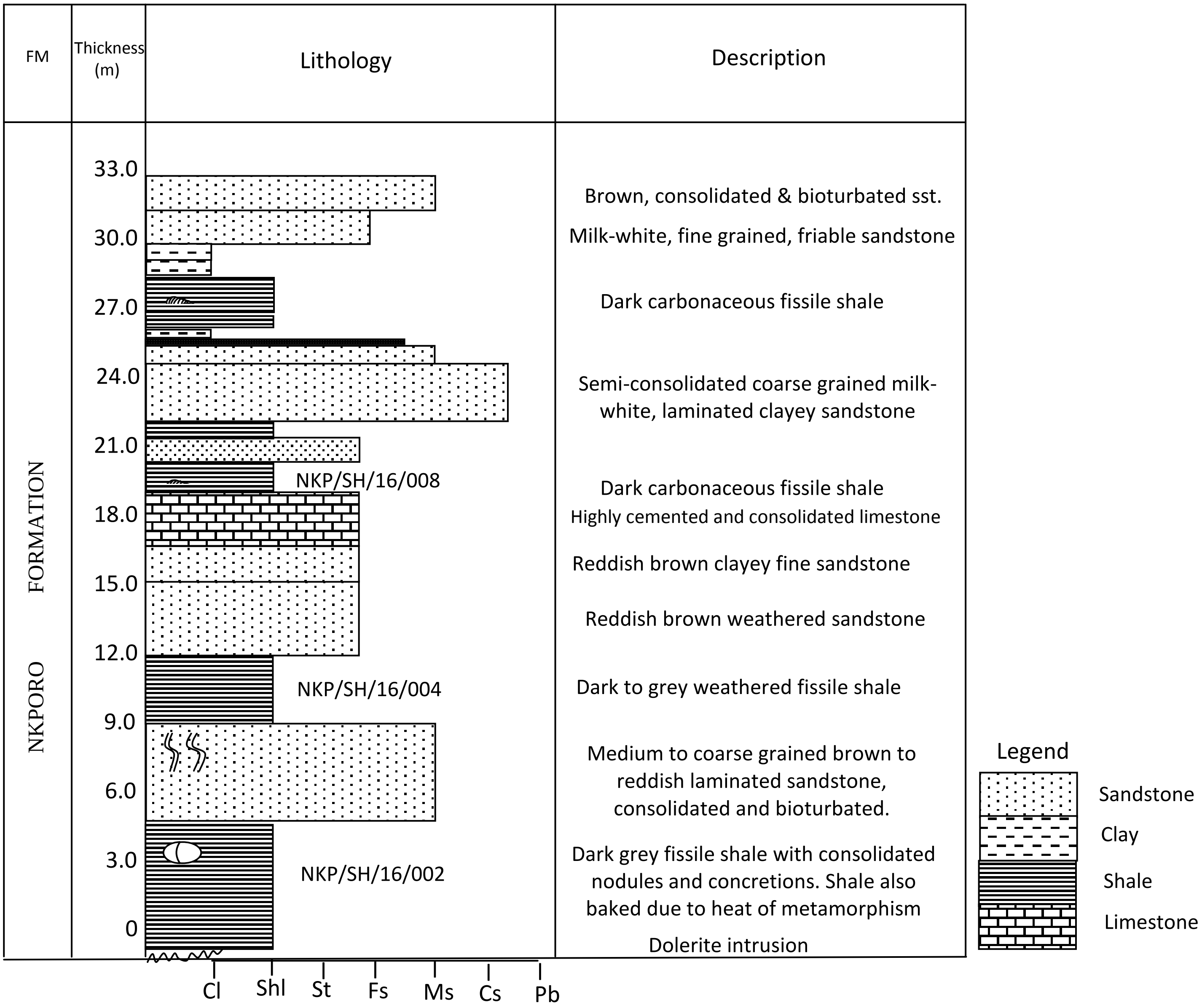

Fig. 4.16a: Lithologic Section at Ochi Stream Section, along Enugu- Port Harcourt Exp. Way, Leru, Abia State.

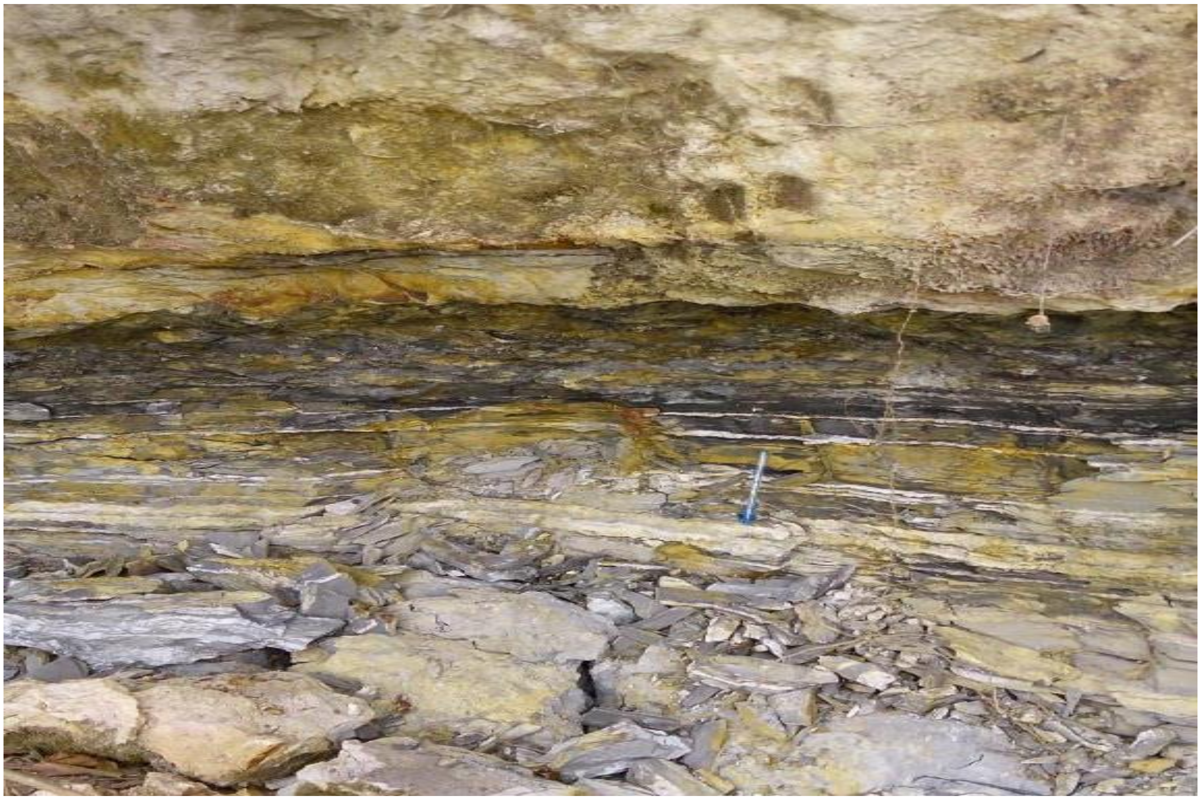

Fig. 4.16b: Photograph of the Outcrop Section at Ochi Stream Section, along Enugu- Port Harcourt Exp. Way, Leru, Abia State.

Location 17

Rock Types: Mudstone, Shale, Siltstone and Sandstone, Pebble

Nature of Outcrop: Oji-Nkwo Stream, along Ugbonabo to Achi Road

Description: The base of the outcrop is dark grey mudstone which has a thickness of about 0.91m (3ft). It is followed by a second unit of 0.30m (1ft) of siltstone. The third unit has a thickness about 0.61m (2ft) of dark grey mudstone. The fourth unit has a thickness of about 0.30m (1ft) of siltstone. The fifth unit has a thickness of about 0.61m (2ft) of dark- grey fissile shale. It was followed by a sharp contact of 1.22m (4ft) of brown, coarse grained, poorly sorted sandstone with mixtures of pebbles and cobbles. This contact separate the Nkporo Shale form the Owelli Sandstone. The top of the outcrop is capped by light brown, semi-consolidated, weathered, fine grained sandstone, having a thickness of about 2.13m (7ft). The total thickness of the outcrop is 6.08m (approx. 20ft) (Fig. 4.17a and b).

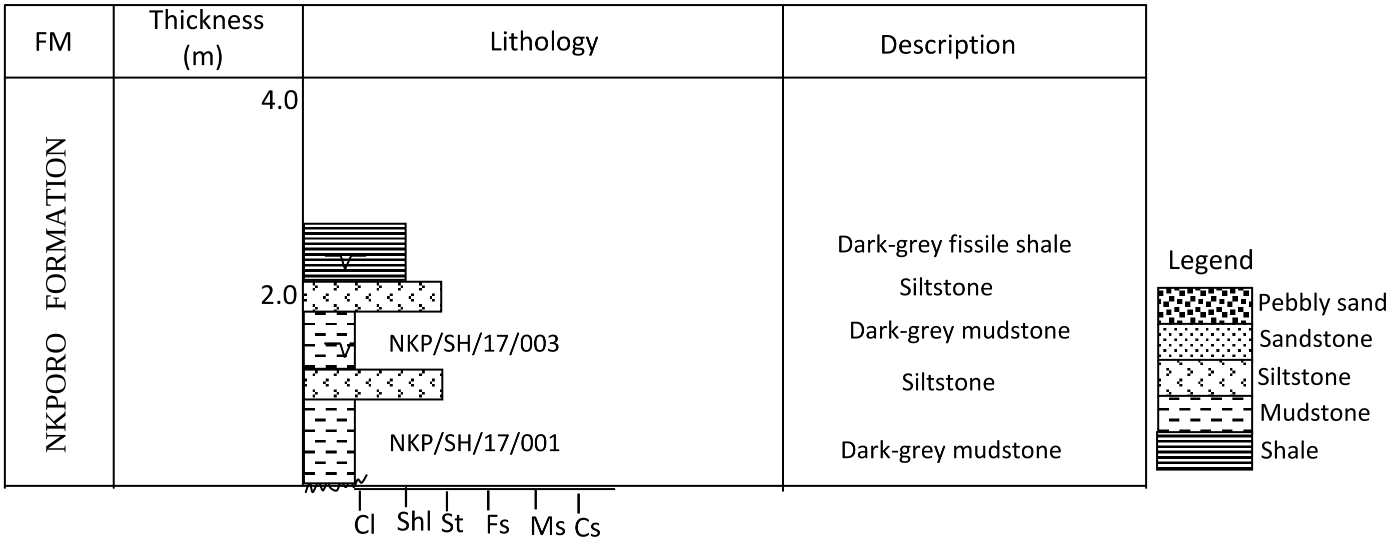

Fig. 4.17a: Lithologic Section at Oji-Nkwo Stream, along Ugbonabo to Achi Road, Enugu State.

Fig. 4.17b: Photograph of the Outcrop Section at Oji-Nkwo Stream, along Ugbonabo to Achi Road, Enugu State.

Location 20

Rock Types: Siltstone and Shale

Nature of Outcrop: Road cut section at Akagbe-Ugwu along portharcourt – Enugu express way.

Description: The base of the outcrop is marked by dark-grey, micaceous, fissile shale which has a thickness of about 2.13m (7ft). It is followed by a thin band of brown siltstone with thickness of about 0.25m (0.82ft). The third unit consists of dark-grey, micaceous, fissile shale having a thickness of about 0.91m (3ft). The fourth unit consists of silt-rich heterolith with shale lenses. This unit has a thickness of about 2.44 (8ft). this is followed by a fifth unit that consists a highly weathered shale, ferruginized, reddish to mottled in colour which has a thickness of about 1.83m (6ft). The top of the outcrop is capped by lateritic, weathered shale overburden which has a thickness of about 3.05m (10ft). The total thickness of the outcrop is 10.61m (34.80ft) (Fig. 4.18a and b).

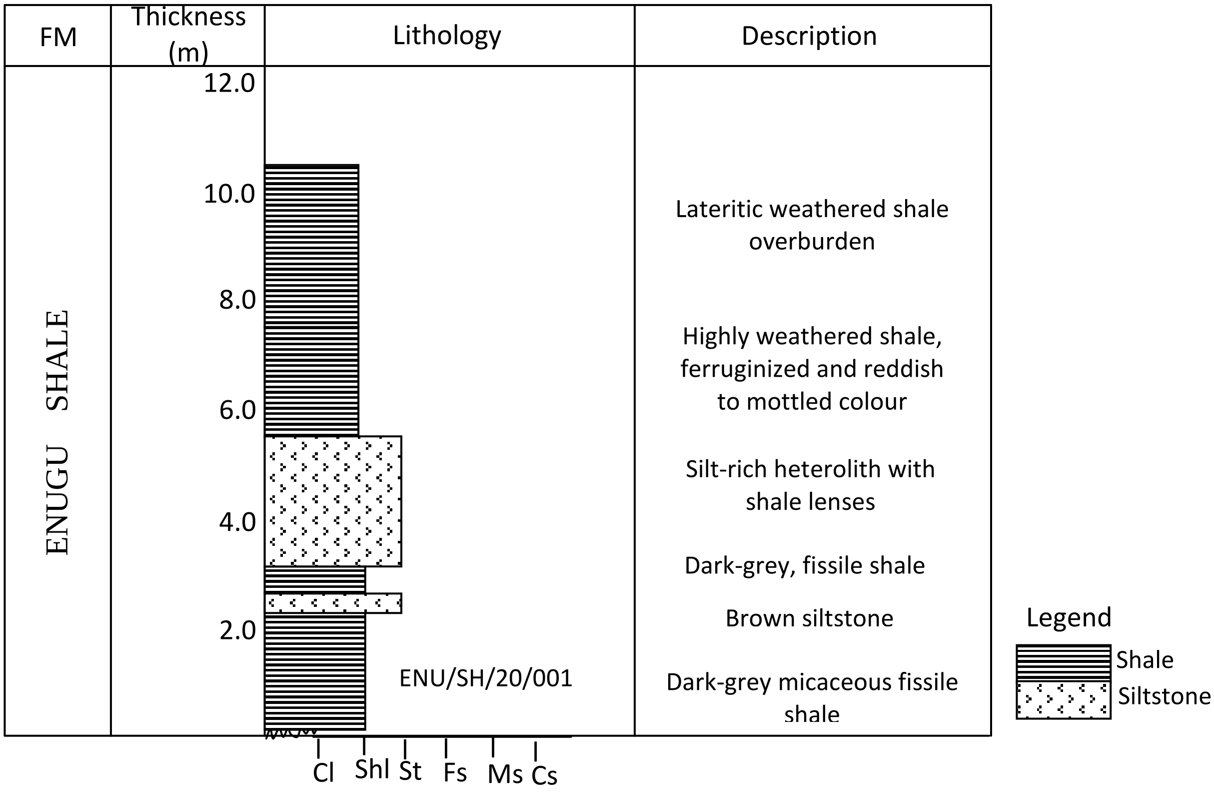

Fig. 4.18a: Lithologic Section at Akagbe-Ugwu, along Port Harcourt to Enugu Exp. Way, Enugu State

Fig. 4.18b: Photograph of the Outcrop Section at Akagbe-Ugwu, along Port Harcourt to Enugu Exp. Way, Enugu State.

Location 21

Rock Types: Siltstone and Shale

Nature of Outcrop: Road cut section along Port Harcourt – Enugu express way at Oshimiri Bus-stop, Akagbe- Ugwu

Description: The base of the outcrop is marked by silt-rich heterolith with clay lenses. There are presence of normal fault, nodules and concretions. It has a thickness of about 1.22m (4ft). It is followed a second unit which consists of dark-grey, micaceous, fissile shale having a thickness of about 2.74m (9ft). The third unit consists of silt-rich heterolith with shale lenses having a thickness of about 1.52m (5ft). The fourth unit consists of dark-grey, micaceous, fissile shale which has a thickness of about 0.91 (3ft). This is followed by a fifth unit that consists of a thin band of siltstone which has a thickness of about 0.30m (1ft). The top of the outcrop is capped by weathered shale overburden which has a thickness of about 3.66m (12ft). The total thickness of the outcrop is 10.35m (approx. 34ft) (Fig. 4.19a and b).

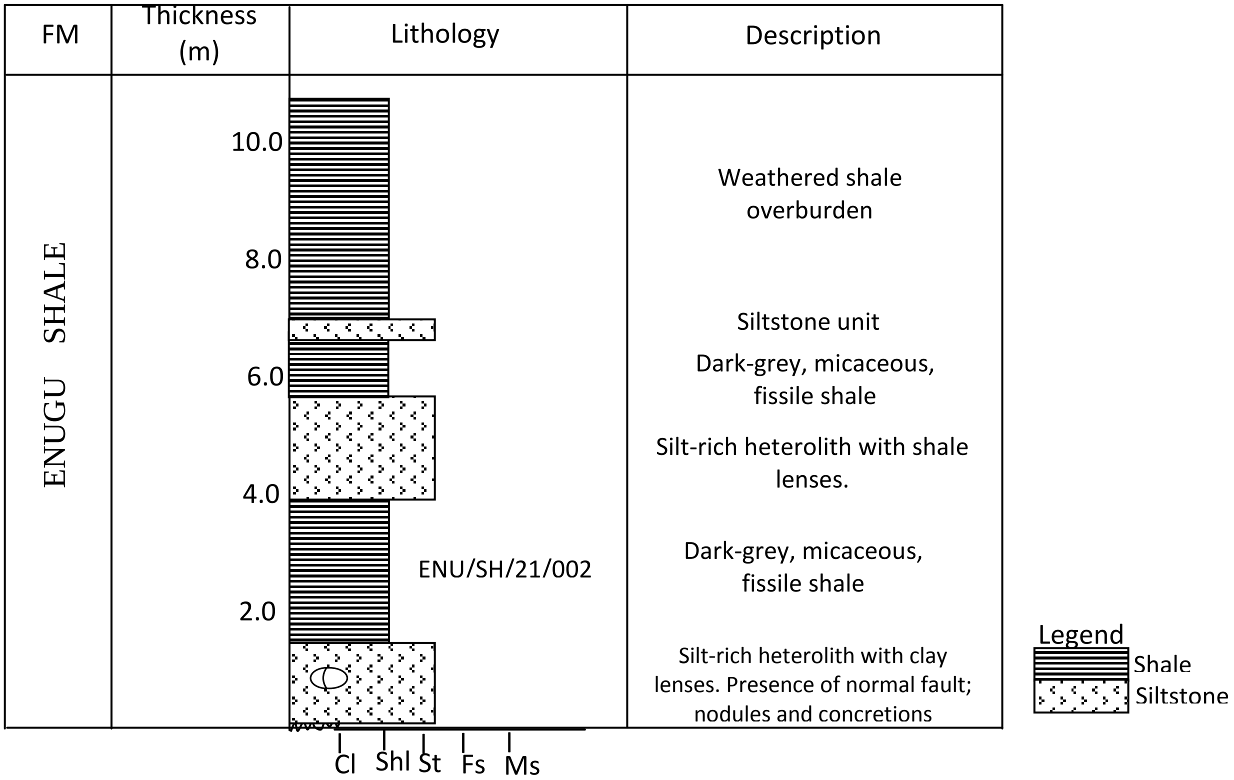

Fig. 4.19a: Lithologic Section at Oshimili Bus-stop, Akagbe-Ugwu, along Port Harcourt to Enugu Exp. Way, Enugu State.

Fig. 4.19b: Photograph of the Outcrop Section at Oshimili Bus-stop, Akagbe-Ugwu, along Port Harcourt to Enugu Exp. Way, Enugu State

Location 22

Rock Types: Siltstone and Shale

Nature of Outcrop: Road cut section along Port Harcourt – Enugu express way by Independence Layout.

Description: The base of the outcrop is marked by dark-grey, micaceous, fissile shale with presence of gypsum efflorescence, ironstone nodules having a thickness of about 3.05m (10ft). It is followed a second unit which consists of thin band of siltstone having a thickness of about 0.40m (1.3ft). The third unit consists of dark-grey, micaceous, fissile shale having a thickness of about 0.30m (1ft). The fourth unit consists of siltstone which has a thickness of about 0.37m (1.2ft). This is followed by a fifth unit which consists of dark-grey, micaceous, fissile shale which has a thickness of about 0.30m (1ft). The sixth unit consists of siltstone having a thickness of about 0.24m (0.8ft). The top of the outcrop is capped by light brown to mottled, weathered shale overburden which has a thickness of about 2.13m (7ft). The total thickness of the outcrop is 6.79m (22.27ft) (Fig. 4.20a and b).

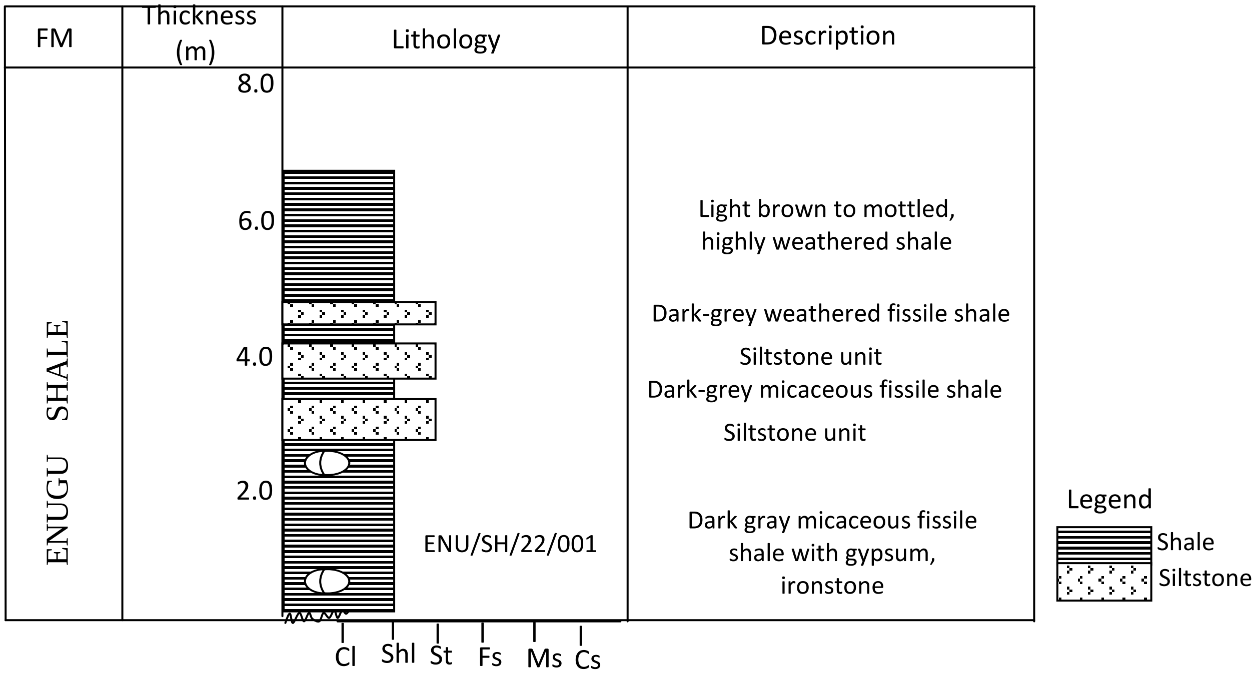

Fig. 4.20a: Lithologic Section at Independence Layout, Akagbe-Ugwu along Enugu to Port Harcourt, Exp. Way, Enugu State

Fig. 4.20b: Photograph of the Outcrop Section at Independence Layout, Akagbe-Ugwu along Enugu to Port Harcourt, Exp. Way, Enugu State

Location 23

Rock Types: Sandstone, Siltstone and Shale

Nature of Outcrop: River cut section at Emene.

Description: The base of the outcrop is marked by dark-grey, carbonaceous, fissile shale with presence of nodules having a thickness of about 4.57m (15ft). It is followed a second unit which consists of thin band of siltstone having a thickness of about 0.30m (1ft). The third unit consists of dark-grey, carbonaceous, fissile shale having a thickness of about 1.22m (4ft). The fourth unit which is the top of the outcrop is capped by weathered, brown, fine grained, moderately sorted sandstone which serves as overburden has a thickness of about 3.35m (11ft). The total thickness of the outcrop is 9.44m (30.96ft) (Fig. 4.21a and b).

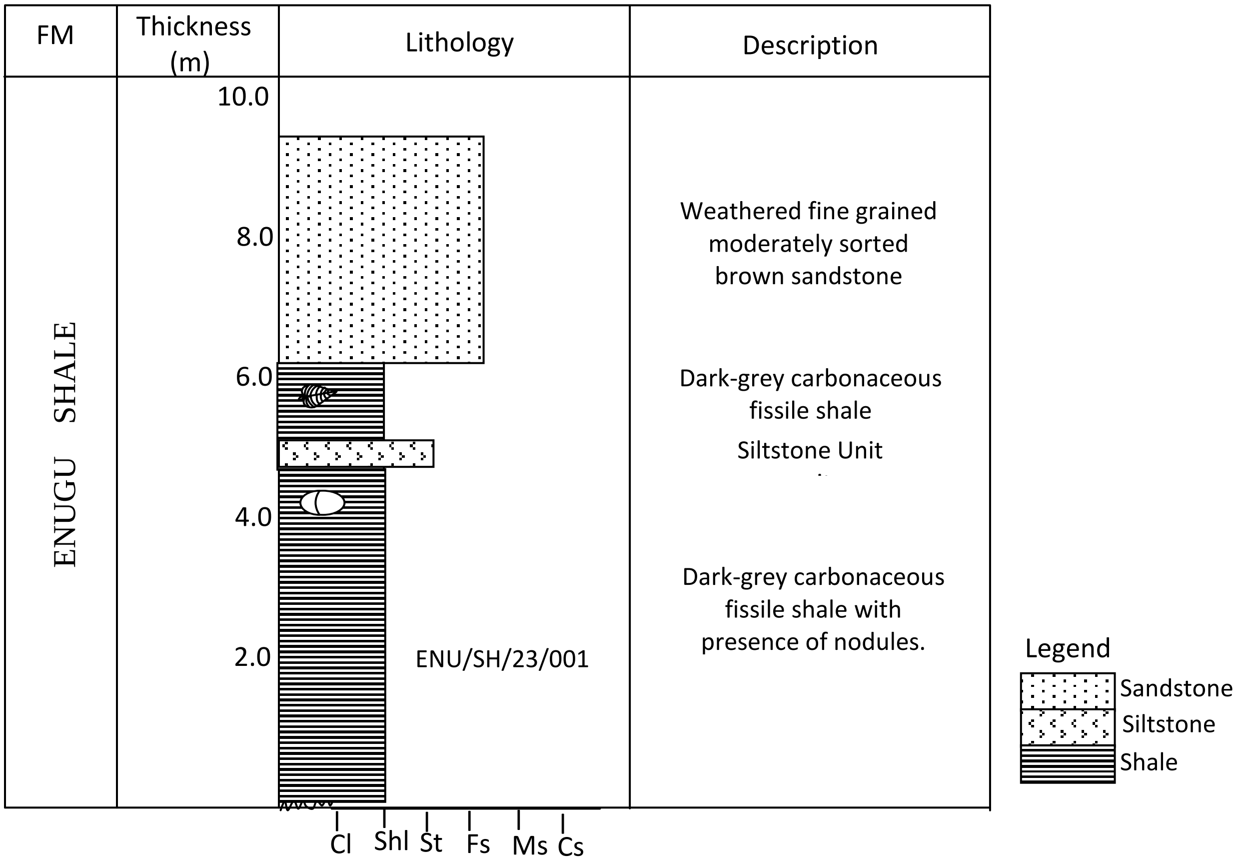

Fig. 4.21a: Lithologic Section at Emene River, Emene, Enugu State

Fig. 4.21b: Photograph of the Outcrop Section at Emene River, Emene, Enugu State

Location 24

Rock Types: Clay and Shale

Nature of Outcrop: Borehole Section at De Branch Suite and Garden, New Haven, Enugu

Description: The base of the well is dark grey fissile shale having a thickness of about 5.49m (18ft). The second unit has a thickness of about 4.57m (15ft) of mottled clay. The third unit has a thickness about 3.66m (12ft) of weathered shale. The total thickness of the well section is 13.72m (45ft) (Fig. 4.22).

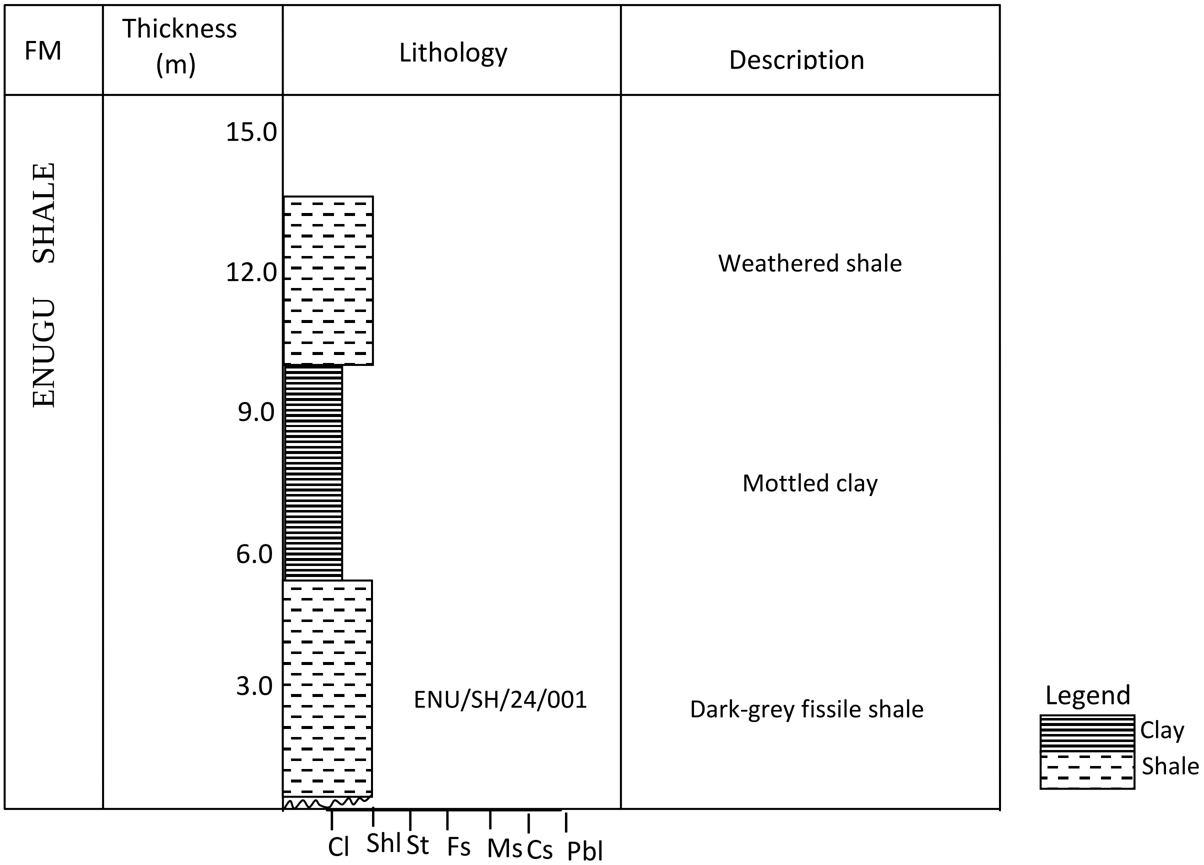

Fig. 4.22: Lithologic Section at De Branch Suite and Garden, New Haven, Enugu State

Location 25

Rock Types: Shale, Siltstone and Mudstone

Nature of Outcrop: Road cut section along Enugu-Onitsha Exp. Way after Trans-ekwulu flyover.

Description: The base of the outcrop is dark grey, fissile shale with presence of nodules and concretions which have a thickness of about 1.98m (6.5ft). It is followed by a thin band of siltstone unit of about 0.30m (1ft). The third unit has a thickness about 1cm (0.39inch) of dark-grey, fissile shale. The fourth unit is 0.29m (0.95ft) of light-brown siltstone. This is followed by 6.40m (21ft) of silt-rich heterolith. There is also presence of fissile shale. The sixth unit has a thickness of about 2.13m (7ft) of dark-grey mudstone, followed by 1.83m (6ft) of another silt-rich heterolith. The eighth unit consists of 1.22m (4ft) of milk-white, clayey siltstone. The top of the outcrop is capped by weathered laterized shale, having a thickness of about 2.13m (7ft). The total thickness of the outcrop is 16.29m (53.43ft) (Fig. 4.23a and b).

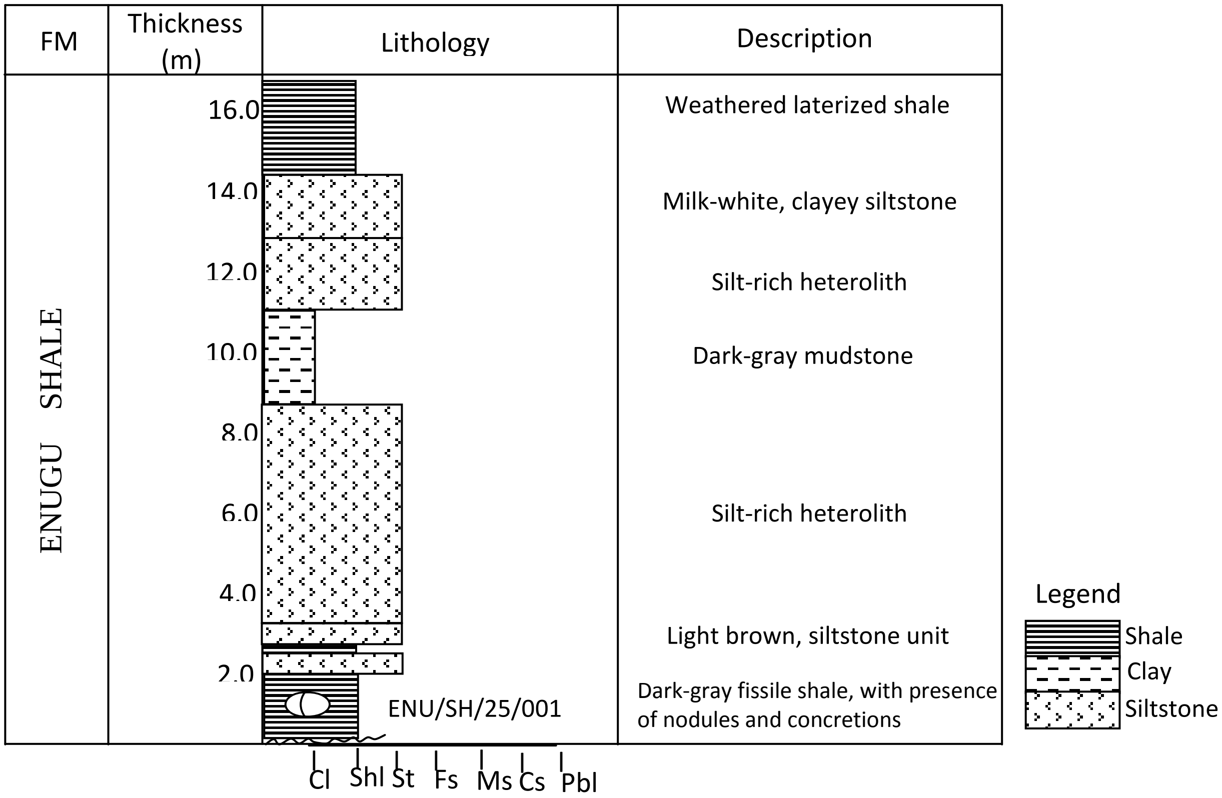

Fig. 4.23a: Lithologic Section after Trans-Ekulu, along Enugu to Onitsha Exp. Way, Enugu State

Fig. 3.23b: Photograph of the Outcrop Section after Trans-Ekulu, along Enugu to Onitsha Exp. Way, Enugu State

Location 26

Rock Types: Shale and Siltstone

Nature of Outcrop: Road cut section along Enugu-Onitsha Exp. Way by Aluson flling station.

Description: The outcrop has alternating layers of dark grey, fissile shale and siltstone with thickness of about 14.33m (47ft). It is followed by a thick bed of silt-rich heterolith of about 6.10m (20ft). After the heterolith silt-rich layer come another alternating layers of dark grey, fissile shale and siltstone having a thickness of about 7.57m (28.11ft). The top of the outcrop is capped by weathered laterized shale, having a thickness of about 3.39m (11.12ft). The total thickness of the outcrop is 31.39m (102.96ft) (Fig. 4.24a and b).

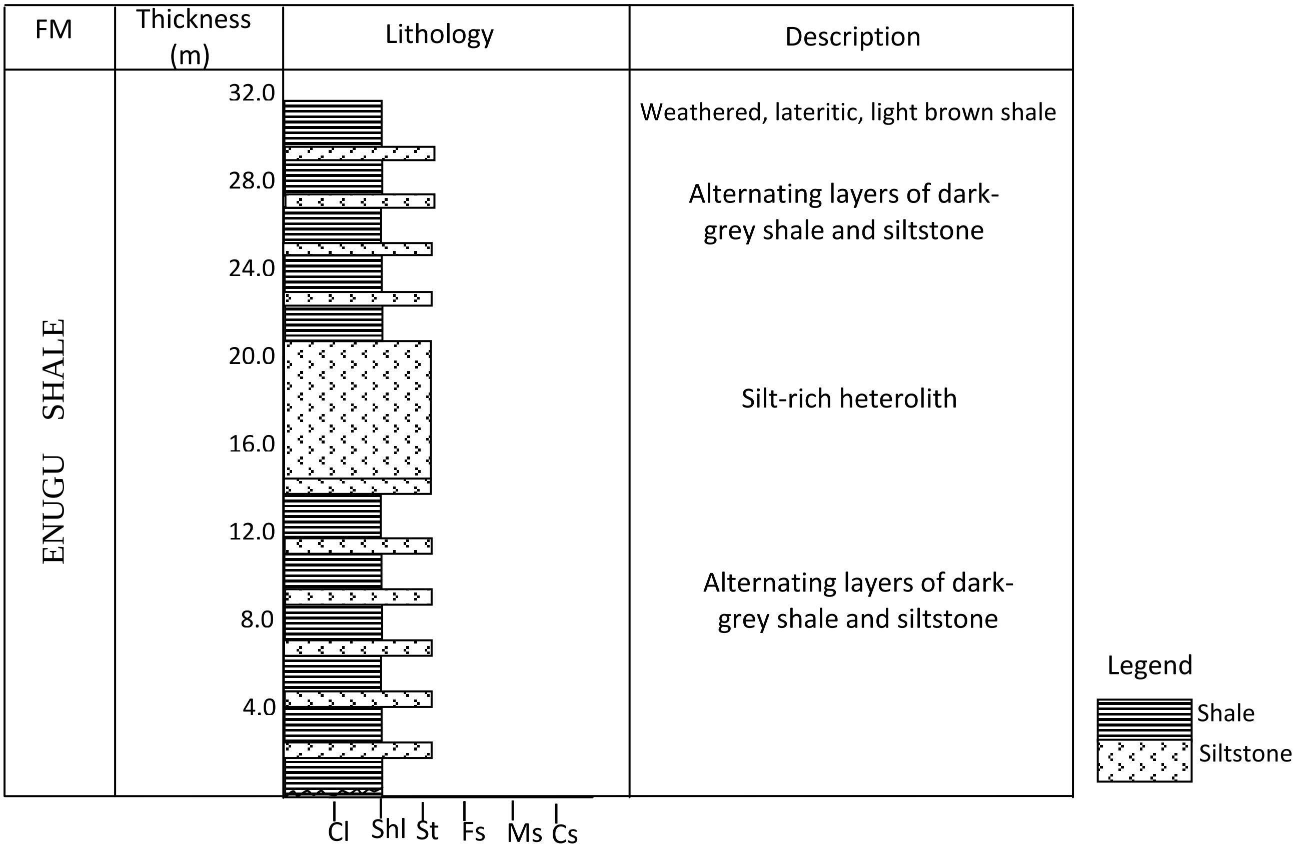

Fig. 4.24a: Lithologic Section at Aluson Petrol Station, along Enugu to Onitsha Exp. Way, Enugu State

Fig. 4.24b: Photograph of the Outcrop Section at Aluson Petrol Station, along Enugu to Onitsha Exp. Way, Enugu State

Location 27

Rock Types: Shale, Siltstone and Sandstone

Nature of Outcrop: Ojume Stream Section, Ikem-Uruaram Town

Description: The base of the outcrop is dark grey fissile shale having a thickness of about 3.05m (10ft). The second unit has a thickness of about 1.22m (4ft) of milk-white consolidated siltstone. In this unit, there is presence of bioturbation. The third unit has a thickness about 1.83m (6ft) of dark grey fissile shale. The top of the outcrop is capped by weathered, medium grained sandstone, with presence of siltstone and sandstone boulders. There is also presence of vesicular textures. The thickness of the unit is about 11.59m (38ft). The total thickness of the outcrop is 17.69m (58.02ft) (Fig. 4.25a and b).

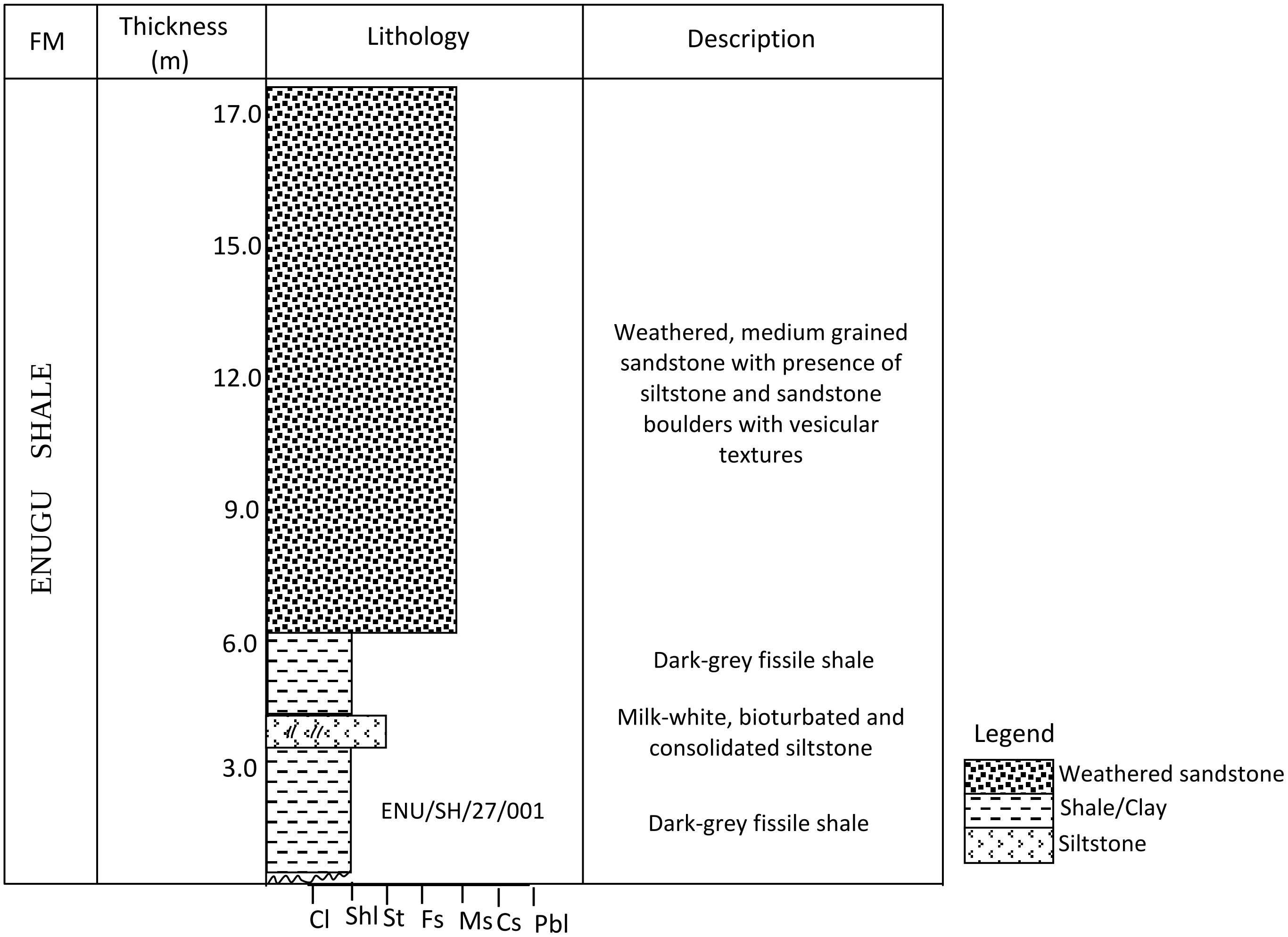

Fig. 4.25a: Lithologic Section at Ojume Stream, Ikem-Uruaram, Enugu State

Fig. 4.25b: Photograph of the Outcrop Section at Ojume Stream, Ikem-Uruaram, Enugu State

4.2 Geologic Map Interpretation

The geologic map of the study area is located within latitudes 5° 30' N and 7° 05' N and longitudes 7° 22' E and 8° 00' E, covering a total area of about 214km^2 was produced on a scale of 1:100,000. The Study Area comprises of two Formations namely; Nkporo Formation and Enugu Shale which were mappped during the field.

Outcrop of the Nkporo Formation are found in Nkporo, Item, Ndi-Okorie and Biakpan areas and some part of Ohafia areas which include Abia, Akanu, Eziafor, communities. It also covers most part of Nguzu-Edda in Afikpo South L.G.A of Ebonyi State. Nkporo Formation is found at the base of the Nkporo Group. This formation is easily recognized by the greyish- black mudstone sometimes fissile in nature. Seventeen outcrop locations were studied within Nkporo Formation. The Enugu Shale covers most parts of Enugu areas and also some parts of Ezimo, Eha Ndiagu, Mbu and Ikem-Uruaram areas. Enugu Shale covers at the middle to the topmost portion of the geologic map. This formation is easily recognized by its dary-grey colour mostly fissile in nature. The formation is basically nosing downwards.

The highest contour on the map is indicated as 500ft. The profile reveals an undulating topography. The geologic map also contains major roads, outcrop locations, and streams/rivers. Legends were also used to identify the lithologic units and other significant features described on the map (Fig. 4.26).

4.3 Source Rock Analysis

4.3.1 Geochemical Analysis

In order to evaluate the organic carbon content and source rock maturity different factors including organic matter richness, generating potentialities, type of organic matter and thermal maturation and expulsion potentials must be achieved. Twenty-five (25) shale samples of the Nkporo Group (Nkporo Formation and Enugu Shale) were discussed based on Hydrocarbon Analyzer with Kinetics (HAWK) pyrolysis data and Total organic carbon (Toc) (Table 4.1a and 4.1b).

4.3.1.1 Organic Matter Richness

The Total organic carbon (TOC) of the shale samples of the Nkporo Formation ranges from 0.41-3.54 wt% with average of 1.53 wt% which indicates a good source rock. The Enugu Shale samples ranges from 0.53-3.39 wt%, with average of 2.03 wt% (Table 4.2a and b). This average value indicates a very source rock (Herdberg and Moody, 1979; Hunt, 1979; Peters and Cassa, 1994; El Nady *et al.*, 2015). Total organic carbon (TOC) value of 0.5wt% is the threshold value required for a potential sources rock to generate hydrocarbon.

The amount of free hydrocarbons (gas and oil) in the sample, S1 and the amount of hydrocarbons generated through thermal cracking of nonvolatile organic matter, S2 for Nkporo Formation is poor which has an average of 0.07 and 0.05 respectively (Table 4.2a). The average value of S1 an S2 of Enugu Shale samples are 0.09 and 1.92 respectively. These values indicate that Enugu Shale is a poor quality source rock for generation of hydrocarbon (Table 4.2b). This conclusion is confirmed by the result of the plot of S2 versus TOC (wt %) (Fig. 4.27a and b) (Espitalié *et al.*, 1985; El Nady *et al.*, 2015).

Table 4.1a: Results of Geochemical Analysis of Nkporo Shale

Sample No.	FM	Sample Type	Percent Carbonate (wt%)	Leco TOC (wt%)	HAWK S1 (mg HC/g)	HAWK S2 (mg HC/g)	HAWK S3 (mg CO$_2$/g)	HAWK Tmax (°C)	Calculated %Ro (RE TMAX)	Hydrogen Index (S2x100/TOC)	Oxygen Index (S3x100/TOC)	S2/S3 Conc. (mg HC/mg CO$_2$)	Bituminous Index S1/TOC	Genetic Potential S1+S2	Production Index (S1/(S1+S2)
NKP/01	Nkporo	Outcrop	27.07	1.24	0.05	0.44	0.79	436	0.69	35	64	1	0.04	0.49	0.10
NKP/02	Nkporo	Outcrop	5.70	0.41	0.13	0.38	1.59	418	0.36	94	392	0	0.32	0.51	0.25
NKP/03	Nkporo	Outcrop	2.46	3.54	0.10	4.40	0.37	434	0.65	124	10	12	0.03	4.5	0.02
NKP/04	Nkporo	Outcrop	6.08	1.69	0.06	0.69	0.36	429	0.56	41	21	2	0.04	0.75	0.08
NKP/06	Nkporo	Outcrop	6.48	1.43	0.05	0.51	0.32	430	0.58	36	22	2	0.03	0.56	0.09
NKP/07	Nkporo	Outcrop	2.78	2.42	0.10	3.06	0.31	434	0.65	126	13	10	0.04	3.16	0.03
NKP/08	Nkporo	Outcrop	10.05	1.64	0.04	1.63	0.86	441	0.78	99	52	2	0.02	1.67	0.02
NKP/09	Nkporo	Outcrop	8.21	1.48	0.05	0.27	0.36	426	0.51	18	24	1	0.03	0.32	0.16
NKP/10	Nkporo	Outcrop	2.96	0.44	0.03	0.08	0.21	426	0.51	18	47	0	0.07	0.11	0.27
NKP/12	Nkporo	Outcrop	12.28	2.39	0.08	0.74	0.78	423	0.45	31	33	1	0.03	0.82	0.10
NKP/13	Nkporo	Outcrop	12.15	1.27	0.05	0.38	0.27	426	0.51	30	21	1	0.04	0.43	0.12
NKP/14	Nkporo	Outcrop	6.54	1.40	0.04	0.28	0.54	421	0.42	20	39	1	0.03	0.32	0.13
NKP/15	Nkporo	Outcrop	4.89	0.51	0.02	0.10	0.35	433	0.63	20	68	0	0.04	0.12	0.17
NKP/16/002	Nkporo	Outcrop	5.74	1.53	0.10	1.55	0.20	441	0.78	101	13	8	0.07	1.65	0.06
NKP/16/004	Nkporo	Outcrop	5.19	2.04	0.06	1.96	0.29	441	0.78	96	14	7	0.03	2.02	0.03
NKP/16/008	Nkporo	Outcrop	2.86	2.13	0.06	1.94	0.24	437	0.71	91	11	8	0.03	2	0.03
NKP/17/001	Nkporo	Outcrop	11.32	0.67	0.06	0.53	0.61	443	0.81	79	91	1	0.09	0.59	0.10
NKP/17/003	Nkporo	Outcrop	6.70	1.38	0.19	1.71	0.22	443	0.81	124	16	8	0.14	1.9	0.10

Table 4.1b: Results of Geochemical Analysis of Enugu Shale

Sample No.	FM	Sample Type	Percent Carbonate (wt%)	Leco TOC (wt%)	HAWK S1 (mg HC/g)	HAWK S2 (mg HC/g)	HAWK S3 (mg CO_2/g)	HAWK Tmax (°C)	Calculated %Ro (RE TMAX)	Hydrogen Index (S2x100/TOC)	Oxygen Index (S3x100/TOC)	S2/S3 Conc. (mg HC/mg CO_2)	Bituminuos Index S1/TOC	Generating Potential S1+S2	Production Index (S1/(S1+S2)
ENU/20	Enugu	Outcrop	7.80	3.39	0.18	2.54	0.31	430	0.58	75	9	8	0.05	2.72	0.07
ENU/21	Enugu	Outcrop	4.15	2.30	0.09	1.17	0.49	431	0.60	51	21	2	0.04	1.26	0.07
ENU/22	Enugu	Outcrop	8.35	1.58	0.06	1.13	0.23	443	0.81	72	15	5	0.04	1.19	0.05
ENU/23	Enugu	Outcrop	9.11	0.95	0.04	0.52	0.20	441	0.78	55	21	3	0.04	0.56	0.07
ENU/24	Enugu	Borehole	4.91	2.32	0.09	3.97	0.26	442	0.80	171	11	15	0.04	4.06	0.02
ENU/25	Enugu	Outcrop	4.15	3.15	0.10	3.76	0.29	438	0.72	119	9	13	0.03	3.86	0.03
ENU/27	Enugu	Outcrop	5.01	0.53	0.05	0.36	0.24	441	0.78	68	45	2	0.09	0.41	0.12

Table 4.2a: Total Organic Carbon, S1 and S2 of the analysed Nkporo Formation Samples

Sample No.	Formation	Sample Type	TOC (wt%)	S1	S2
NKP/01	Nkporo	Outcrop	1.24	0.05	0.44
NKP/02	Nkporo	Outcrop	0.41	0.13	0.38
NKP/03	Nkporo	Outcrop	3.54	0.10	4.40
NKP/04	Nkporo	Outcrop	1.69	0.06	0.69
NKP/06	Nkporo	Outcrop	1.43	0.05	0.51
NKP/07	Nkporo	Outcrop	2.42	0.10	3.06
NKP/08	Nkporo	Outcrop	1.64	0.04	1.63
NKP/09	Nkporo	Outcrop	1.48	0.05	0.27
NKP/10	Nkporo	Outcrop	0.44	0.03	0.08
NKP/12	Nkporo	Outcrop	2.39	0.08	0.74
NKP/13	Nkporo	Outcrop	1.27	0.05	0.38
NKP/14	Nkporo	Outcrop	1.40	0.04	0.28
NKP/15	Nkporo	Outcrop	0.51	0.02	0.10
NKP/16/002	Nkporo	Outcrop	1.53	0.10	1.55
NKP/16/004	Nkporo	Outcrop	2.04	0.06	1.96
NKP/16/008	Nkporo	Outcrop	2.13	0.06	1.94
NKP/17/001	Nkporo	Outcrop	0.67	0.06	0.53
NKP/17/003	Nkporo	Outcrop	1.38	0.19	1.71
		Average	1.53	0.07	1.15

Table 4.2b Average of Total Organic Carbon Result of Enugu Shale

Sample No.	Formation	Sample Type	TOC (wt%)	S1	S2
ENU/20	Enugu	Outcrop	3.39	0.18	2.54
ENU/21	Enugu	Outcrop	2.30	0.09	1.17
ENU/22	Enugu	Outcrop	1.58	0.06	1.13
ENU/23	Enugu	Outcrop	0.95	0.04	0.52
ENU/24	Enugu	Borehole	2.32	0.09	3.97
ENU/25	Enugu	Outcrop	3.15	0.10	3.76
ENU/27	Enugu	Outcrop	0.53	0.05	0.36
		Average	2.03	0.09	1.92

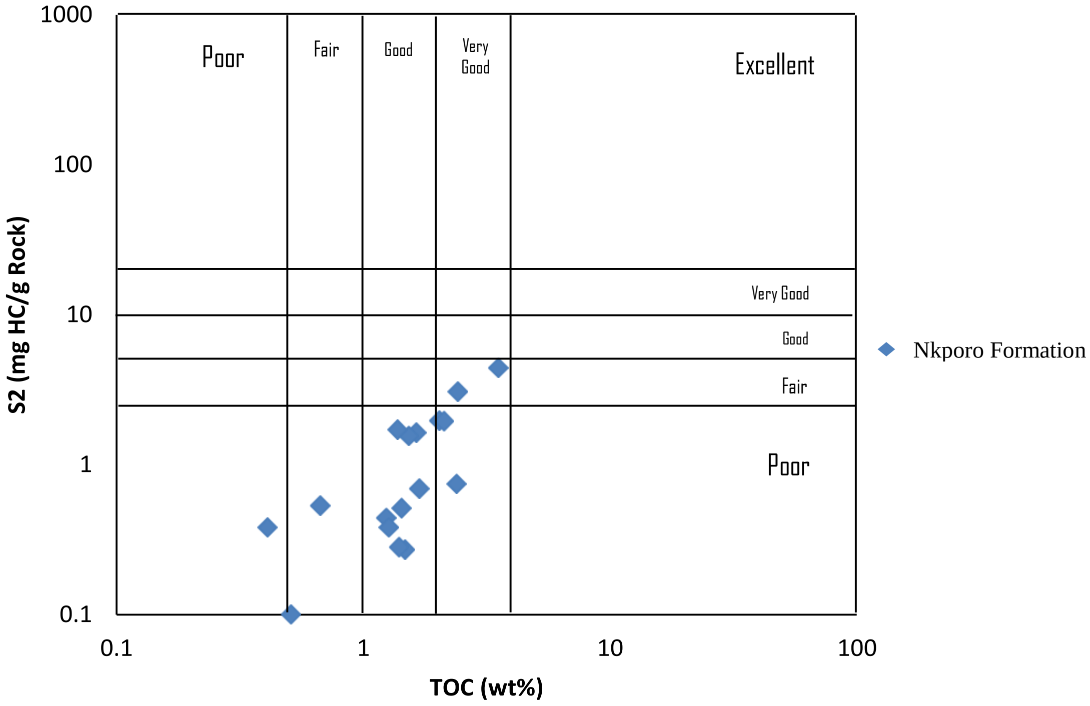

Fig. 4.27a: Plot of S2 versus TOC (wt%) demonstrate the quality and quantity of hydrocarbon of Nkporo Formation Samples (Espitalié *et al.* 1985)

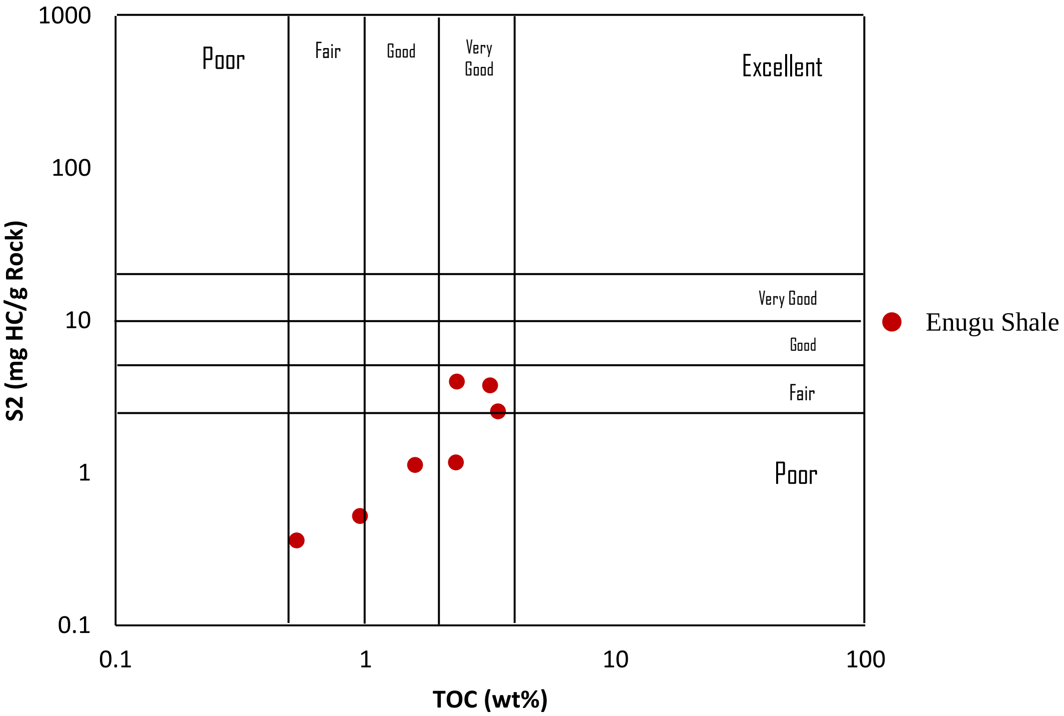

Fig. 4.27b: Plot of S2 versus TOC (wt%) demonstrate the quality and quantity of hydrocarbon of Enugu Shale Samples (Espitalié *et al.* 1985)

4.3.1.2. Generation Potential

The generation potential (GP) is the sum of the values of S1 and S2. According to Hunt, 1996, source rocks with a GP <2, from 2 to 5, from 5 to 10 and >10 are considered poor, fair, good and very good generation potential, respectively. The relationship between (S1 + S2) and TOC (wt. %) (Waples, 1985; El Nady *et al.,* 2015) shows that the Nkporo Formation and the Enugu Shale samples are considered as poor to fair source potential (Fig. 4.28a and b). The average generation potential for Nkporo Formation is 1.22mg/g which indicates a poor source potential (Table 4.3a), while that of Enugu Shale has an average genetic potential of 2.01mg/g which indicates a fair source potential (Table 4.3b). The hydrocarbon yield is derived from the plot of genetic potential, GP against calculated vitrinite reflectance, %Ro which shows that the two samples from Nkporo Formation (NKP/03 and NKP/06) and Enugu Shale (ENU/24 and ENU/25) indicates oil; eight samples from Nkporo Formation (NKP/01, NKP/08, NKP/15, NKP/16/002, NKP/16/004, NKP/16/008, NKP/17/001, NKP/17/001 and NKP/17/003) and three samples from (ENU/22, ENU/23 and ENU/27) indicates gas; another eight samples from Nkporo Formation (NKP/02, NKP/04, NKP/06, NKP/09, NKP/10, NKP/12 and NKP/13) and one sample from Enugu Shale (ENU/21) indicates gas potential; one sample from Enugu Shale (ENU/20) indicates oil potential (Fig. 4.29a and b).

Table 4.3a Results of TOC, Hydrogen Index, HI and Generation Potentials for Nkporo Formation

Sample No.	Formation	Sample Type	Leco TOC (wt%)	Hydrogen Index, HI	GP S1 +S2	Calc. VR %Ro
NKP/01	Nkporo	Outcrop	1.24	35	0.49	0.69
NKP/02	Nkporo	Outcrop	0.41	94	0.51	0.36
NKP/03	Nkporo	Outcrop	3.54	124	4.5	0.65
NKP/04	Nkporo	Outcrop	1.69	41	0.75	0.56
NKP/06	Nkporo	Outcrop	1.43	36	0.56	0.58
NKP/07	Nkporo	Outcrop	2.42	126	3.16	0.65
NKP/08	Nkporo	Outcrop	1.64	99	1.67	0.78
NKP/09	Nkporo	Outcrop	1.48	18	0.32	0.51
NKP/10	Nkporo	Outcrop	0.44	18	0.11	0.51
NKP/12	Nkporo	Outcrop	2.39	31	0.82	0.45
NKP/13	Nkporo	Outcrop	1.27	30	0.43	0.51
NKP/14	Nkporo	Outcrop	1.40	20	0.32	0.42
NKP/15	Nkporo	Outcrop	0.51	20	0.12	0.63
NKP/16/002	Nkporo	Outcrop	1.53	101	1.65	0.78
NKP/16/004	Nkporo	Outcrop	2.04	96	2.02	0.78
NKP/16/008	Nkporo	Outcrop	2.13	91	2	0.71
NKP/17/001	Nkporo	Outcrop	0.67	79	0.59	0.81
NKP/17/003	Nkporo	Outcrop	1.38	124	1.9	0.81
		Average	1.53	65.72	1.22	0.62

Table 4.3b: Results of TOC, Hydrogen Index, HI and Genetic Potentials for Enugu Shale

Sample No.	Formation	Sample Type	Leco TOC (wt%)	Hydrogen Index, HI	GP S1 + S2	Calc. VR %Ro
ENU/20	Enugu	Outcrop	3.39	75	2.72	0.58
ENU/21	Enugu	Outcrop	2.30	51	1.26	0.60
ENU/22	Enugu	Outcrop	1.58	72	1.19	0.81
ENU/23	Enugu	Outcrop	0.95	55	0.56	0.78
ENU/24	Enugu	Borehole	2.32	171	4.06	0.80
ENU/25	Enugu	Outcrop	3.15	119	3.86	0.72
ENU/27	Enugu	Outcrop	0.53	68	0.41	0.78
		Average	2.03	87.29	2.01	0.72

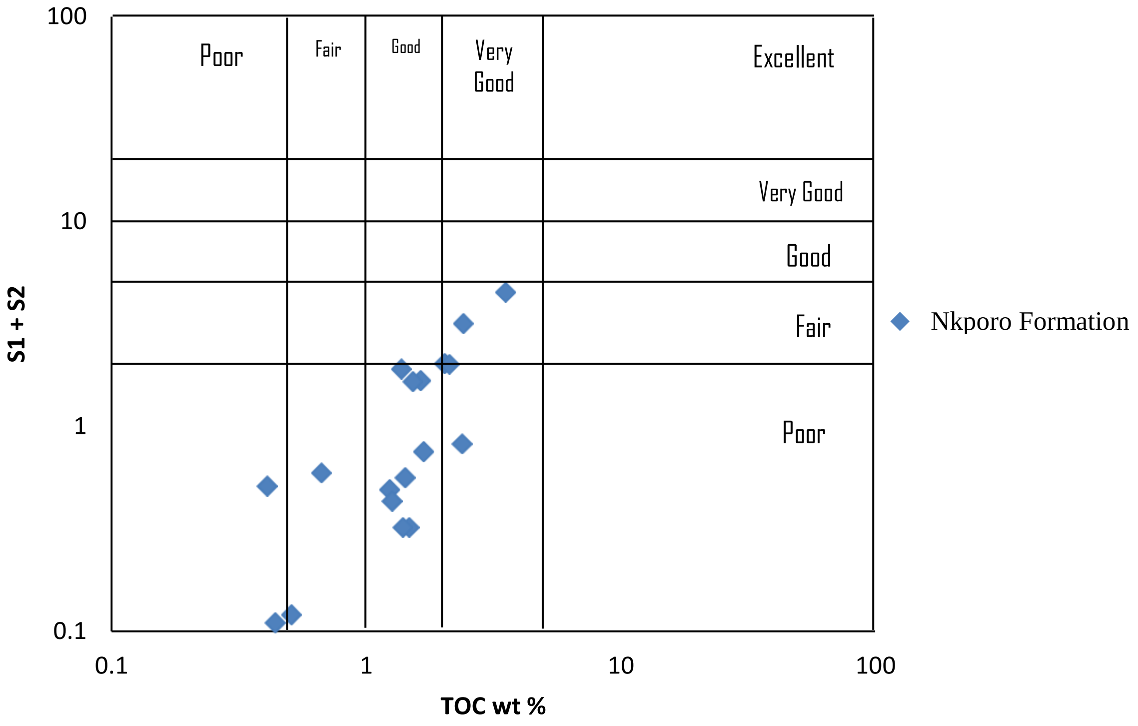

Fig. 4.28a: Plot of (S1 +S2) versus TOC (wt%) to demonstrate the generating potentialities of the Nkporo Formation samples (Waples, 1985)

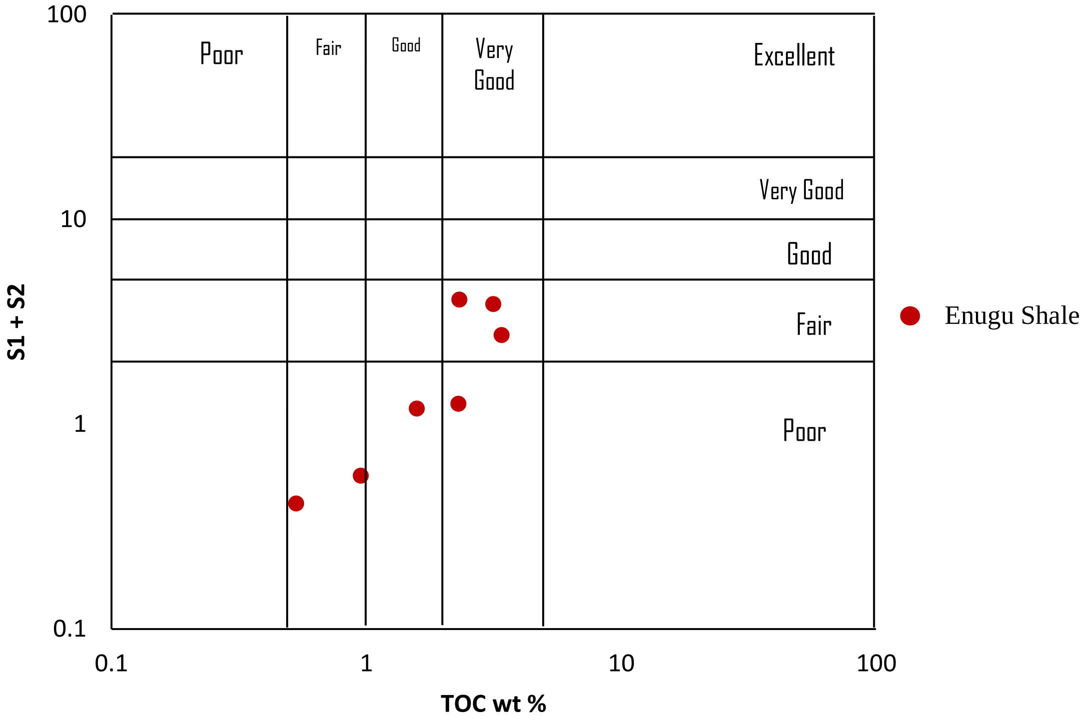

Fig. 4.28b: Plot of (S1 +S2) versus TOC (wt %) to demonstrate the generating potentialities of the Enugu Shale samples (Waples, 1985)

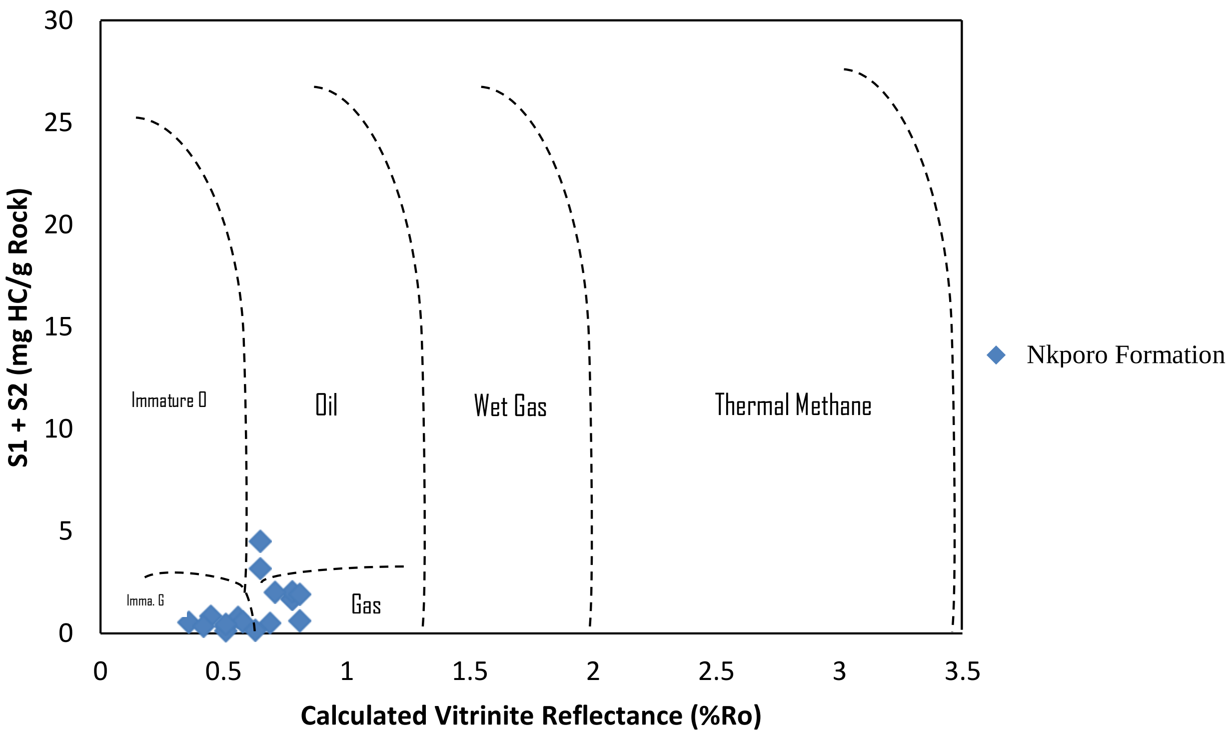

Fig. 4.29a: Plot of GP (S1 + S2) versus Calc. %Ro of the Nkporo Formation samples

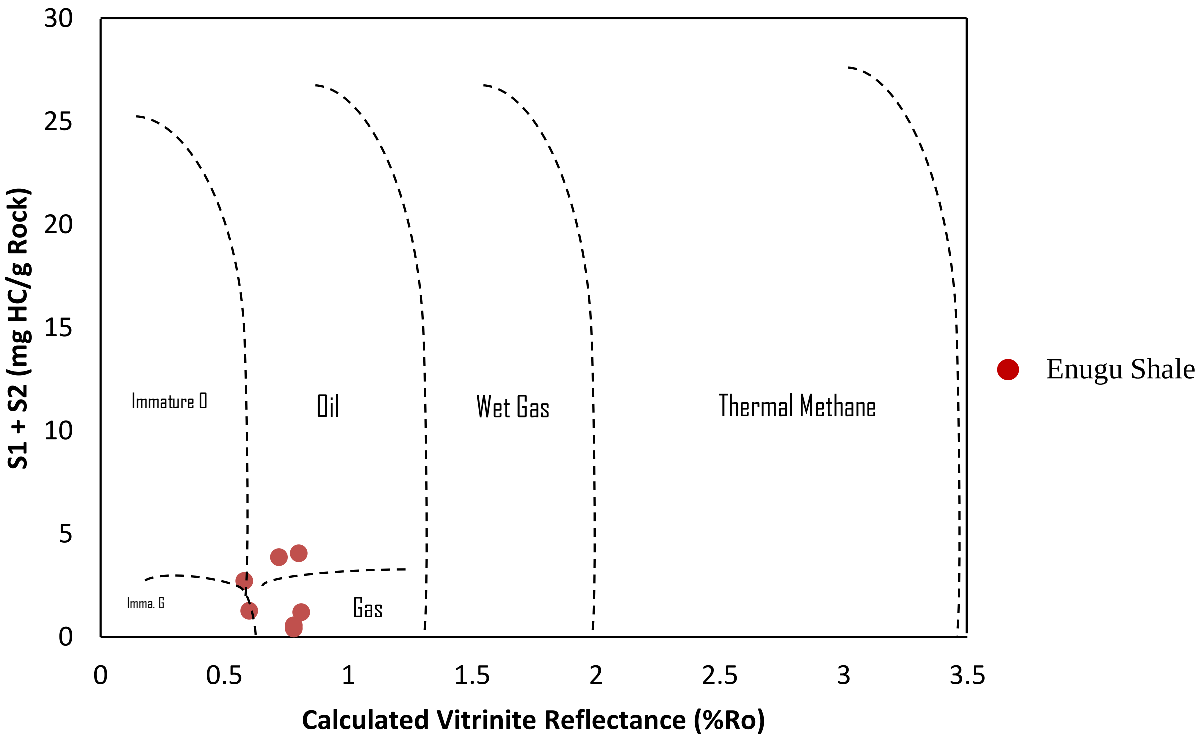

Fig. 4.29b: Plot of GP (S1 + S2) versus Calc. %Ro of the Enugu Shale samples

4.3.1.3 Types of Organic Matter

The type of organic matter of a source rock is essential for the prediction of oil and gas potential. In this study, Langford and Blanc-Valleron kerogen type diagram was used to represents the plot of S2 versus TOC (Fig. 4.30a and b).This diagram shows that the studied samples for Nkporo Formation are characterized by kerogen of type III and type IV having mostly an atomic H/C of <0.7, while that of Enugu Shale are characterized mostly by type III which have an atomic H/C between 0.7 and 1.0.

Based on pyrolysis data, kerogen classification diagrams were constructed using the Hydrogen Index (HI) versus Oxygen Index (OI), which is used to determine the kerogen type (Fig. 4.31a and b). The results show that the analyzed Nkporo Formation samples are of type III and IV kerogen which are predominantly inert, while the analyzed Enugu Shale samples are of type III kerogen which is gas prone. Hydrogen Index, HI for Nkporo Formation and Enugu Shale have an average value of 65.72mg HC/g TOC and 87.2972mg HC/g TOC respectively which indicates gas prone (Table 4.4a and b).

Table 4.4a: Results of TOC, Hydrogen Index, HI and Oxygen Index, OI for Nkporo Formation

Sample No.	Formation	Sample Type	Leco TOC (wt%)	Hydrogen Index, HI	Oxygen Index, OI
NKP/01	Nkporo	Outcrop	1.24	35	64
NKP/02	Nkporo	Outcrop	0.41	94	392
NKP/03	Nkporo	Outcrop	3.54	124	10
NKP/04	Nkporo	Outcrop	1.69	41	21
NKP/06	Nkporo	Outcrop	1.43	36	22
NKP/07	Nkporo	Outcrop	2.42	126	13
NKP/08	Nkporo	Outcrop	1.64	99	52
NKP/09	Nkporo	Outcrop	1.48	18	24
NKP/10	Nkporo	Outcrop	0.44	18	47
NKP/12	Nkporo	Outcrop	2.39	31	33
NKP/13	Nkporo	Outcrop	1.27	30	21
NKP/14	Nkporo	Outcrop	1.40	20	39
NKP/15	Nkporo	Outcrop	0.51	20	68
NKP/16/002	Nkporo	Outcrop	1.53	101	13
NKP/16/004	Nkporo	Outcrop	2.04	96	14
NKP/16/008	Nkporo	Outcrop	2.13	91	11
NKP/17/001	Nkporo	Outcrop	0.67	79	91
NKP/17/003	Nkporo	Outcrop	1.38	124	16
		Average	1.53	65.72	52.83

Table 4.5b Results of TOC, Hydrogen Index, HI and Oxygen Index, OI for Enugu Shale

Sample No.	Formation	Sample Type	Leco TOC (wt%)	Hydrogen Index, HI	Oxygen Index, OI
ENU/20	Enugu	Outcrop	3.39	75	9
ENU/21	Enugu	Outcrop	2.30	51	21
ENU/22	Enugu	Outcrop	1.58	72	15
ENU/23	Enugu	Outcrop	0.95	55	21
ENU/24	Enugu	Borehole	2.32	171	11
ENU/25	Enugu	Outcrop	3.15	119	9
ENU/27	Enugu	Outcrop	0.53	68	45
		Average	2.03	87.29	18.71

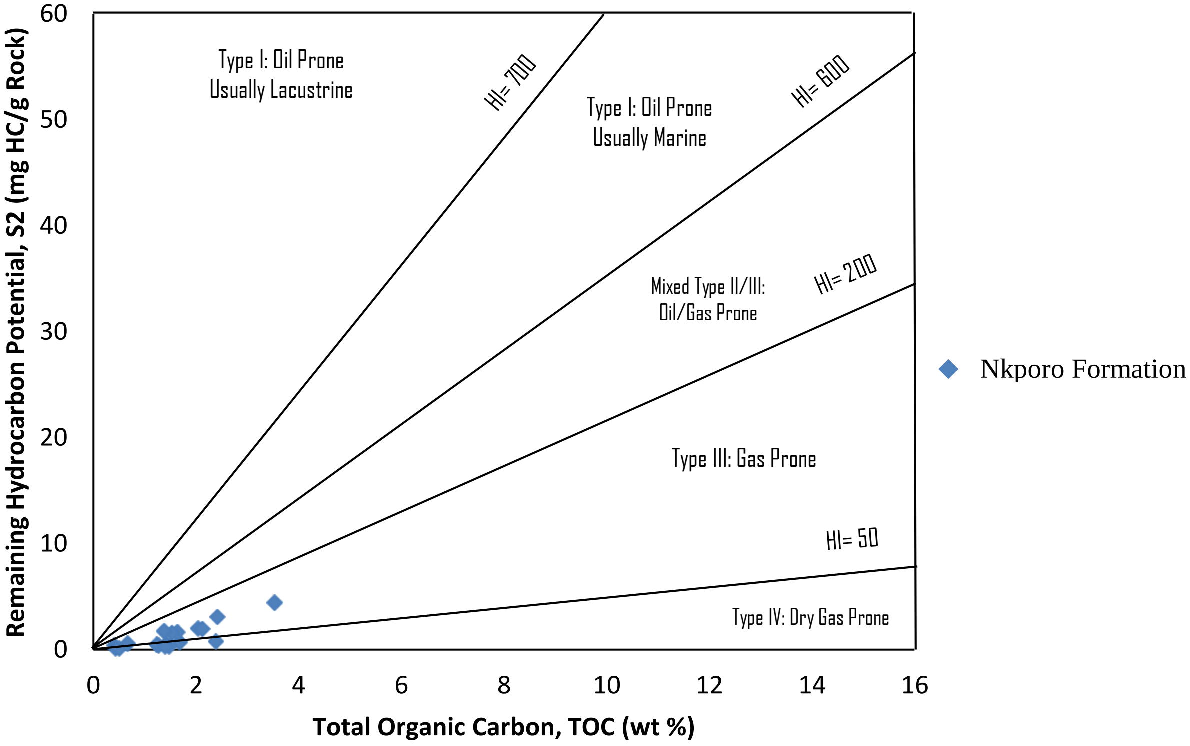

Fig. 4.30a: Plot of S2 versus TOC (wt%) to identify the kerogen quality/ type of hydrocarbon produced from the source rock of the Nkporo Formation (Langford and Blanc-Valleron, 1990).

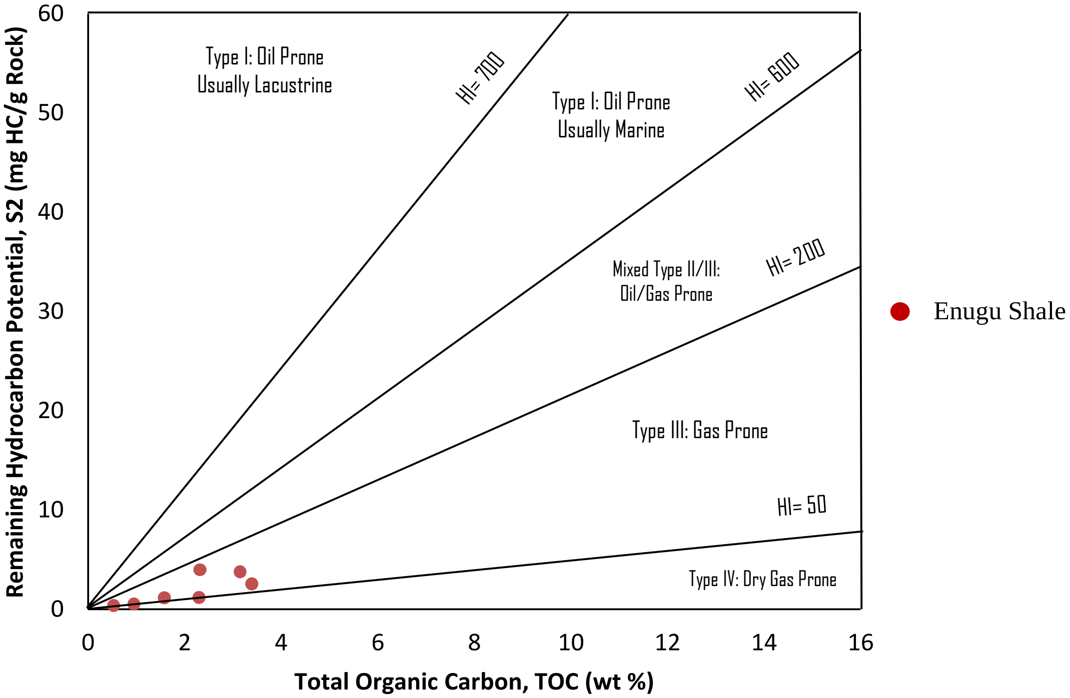

Fig. 4.30b: Plot of S2 versus TOC (wt%) to identify the kerogen quality/ type of hydrocarbon produced from the source rock of the Enugu Shale samples (Langford and Blanc-Valleron, 1990)

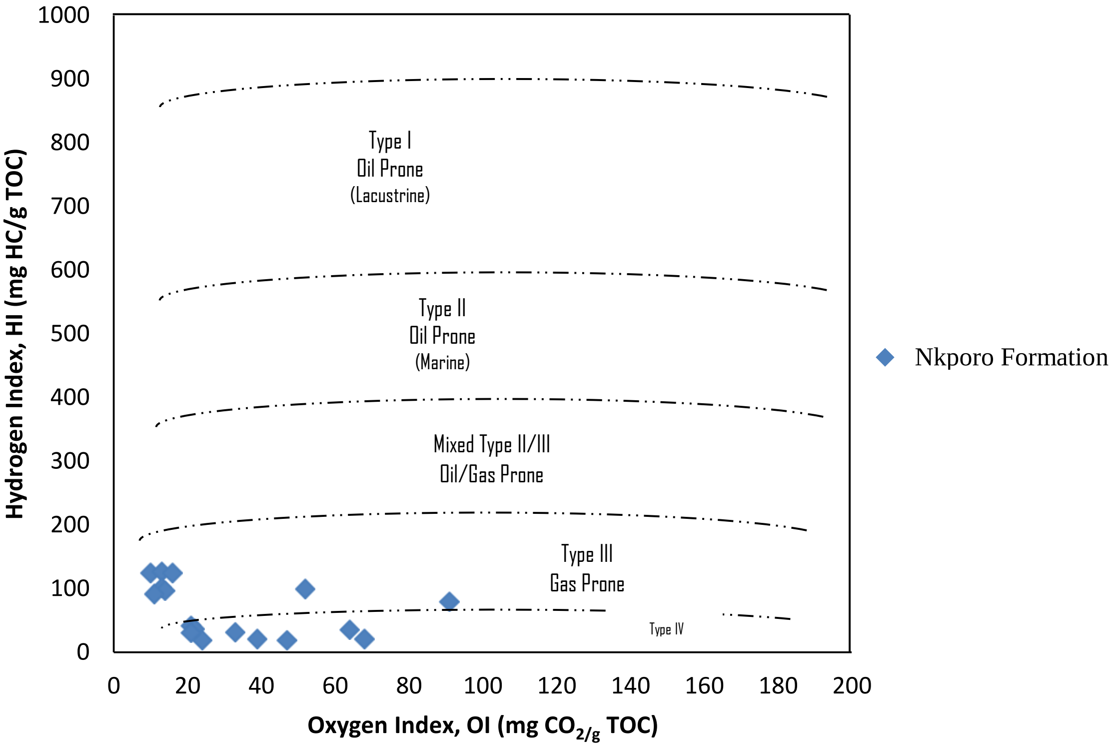

Fig. 4.31a: Plot of Hydrogen Index (HI) versus Oxygen Index (OI) shows the type of kerogen available in the source rock of Nkporo Formation samples (Espitalié et al. 1985)

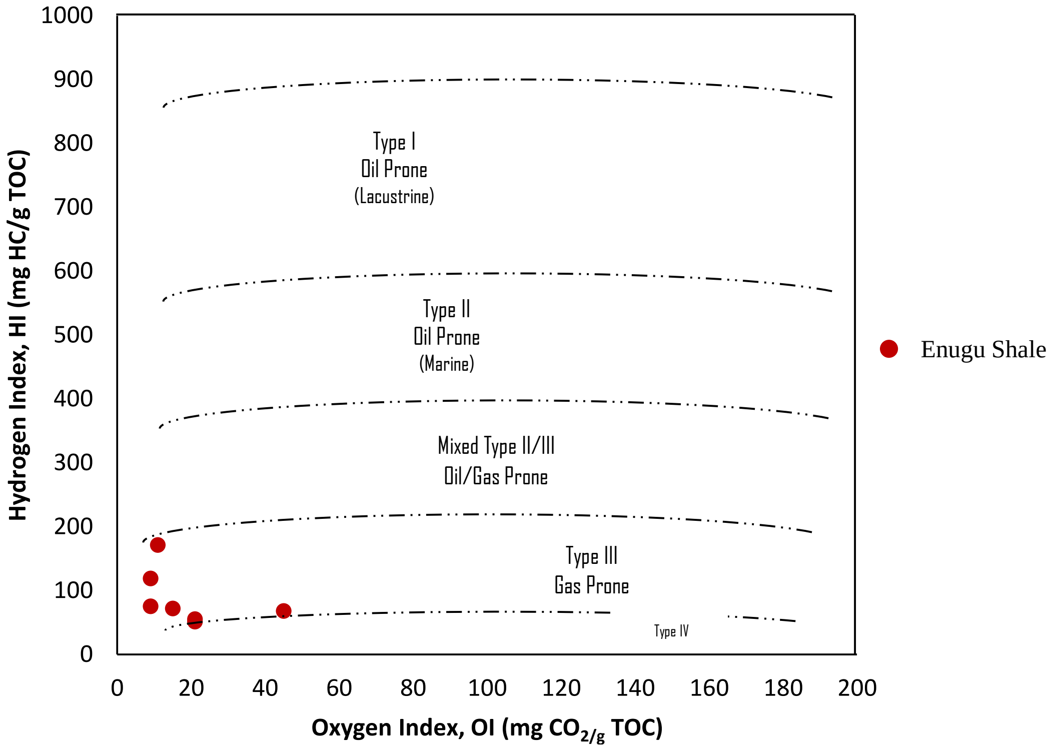

Fig. 4.31b: Plot of Hydrogen Index (HI) versus Oxygen Index (OI) shows the type of kerogen available in the source rock of Enugu Shale samples (Espitalié et al. 1985)

4.3.1.4 Thermal Maturity of Organic Matter

In the present study, the thermal maturity level of the source rocks has been determined by the study of the geochemical parameters as Rock–Eval temperature pyrolysis ‘‘Tmax’’, production index ‘‘PI’’ (Hunt, 1996; Espitalie et al, 1985). Results of Hydrogen Index, HI, Tmax and Production Index, PI for Nkporo Formation and Enugu Shale samples are shown in Table 4.5a and b. Based on pyrolysis data, kerogen classification diagrams were constructed using the Hydrogen Index, HI versus Tmax plot and Hydrogen Index, HI versus calculated vitrinite reflectance was carried out by Espitalie et al, 1985. These plots were used to determine the kerogen type and maturity. The plot of Hydrogen Index, HI versus Tmax show that the analyzed Nkporo Formation samples are ranges from the immature to mature zone of type III and IV kerogen, while the analyzed Enugu Shale samples of the studied area are at mature stage of oil window and also of type III kerogen (Fig. 4.32a and b).

The plot of Hydrogen Index, HI versus calculated vitrinite reflectance shows that the Nkporo Formation samples consist of kerogen which ranges from type III and IV. Some of the samples within the type III kerogen fell into the oil window, while the analyzed Enugu Shale samples of the studied area mostly within the type III kerogen also falls into the oil window (Fig. 4.33a and b).

The plot of Production Index, PI versus Tmax diagram (Peters, 1986; Waples, 1985) shows that most of the Nkporo Formation samples are immature source rocks, while the Enugu Shale samples are mature source rocks except that of sample location ENU/20 and ENU/21 which are marginally mature (Fig. 4.34a and b). The plot of Production Index, PI versus calculated vitrinite reflectance, %Ro shows that studied Nkporo Formation samples range from immature to the oil window, while most of the samples from the Enugu Shale are within the oil window (Fig. 4.35a and b).

Table 4.5a Results of Hydrogen Index, HI, Tmax and Production Index, PI for Nkporo Formation

Sample No.	Formation	Sample Type	Hydrogen Index, HI	Tmax	Production Index, PI	Calc. VR %Ro
NKP/01	Nkporo	Outcrop	35	436	0.10	0.69
NKP/02	Nkporo	Outcrop	94	418	0.25	0.36
NKP/03	Nkporo	Outcrop	124	434	0.02	0.65
NKP/04	Nkporo	Outcrop	41	429	0.08	0.56
NKP/06	Nkporo	Outcrop	36	430	0.09	0.58
NKP/07	Nkporo	Outcrop	126	434	0.03	0.65
NKP/08	Nkporo	Outcrop	99	441	0.02	0.78
NKP/09	Nkporo	Outcrop	18	426	0.16	0.51
NKP/10	Nkporo	Outcrop	18	426	0.27	0.51
NKP/12	Nkporo	Outcrop	31	423	0.10	0.45
NKP/13	Nkporo	Outcrop	30	426	0.12	0.51
NKP/14	Nkporo	Outcrop	20	421	0.13	0.42
NKP/15	Nkporo	Outcrop	20	433	0.17	0.63
NKP/16/002	Nkporo	Outcrop	101	441	0.06	0.78
NKP/16/004	Nkporo	Outcrop	96	441	0.03	0.78
NKP/16/008	Nkporo	Outcrop	91	437	0.03	0.71
NKP/17/001	Nkporo	Outcrop	79	443	0.10	0.81
NKP/17/003	Nkporo	Outcrop	124	443	0.10	0.81
		Average	65.72	432.33	0.10	0.62

Table 4.5b Results of Hydrogen Index, HI, Tmax and Production Index, PI for Enugu Shale

Sample No.	Formation	Sample Type	Hydrogen Index, HI	Tmax	Production Index, PI	Calc. VR %Ro
ENU/20	Enugu	Outcrop	75	430	0.07	0.58
ENU/21	Enugu	Outcrop	51	431	0.07	0.60
ENU/22	Enugu	Outcrop	72	443	0.05	0.81
ENU/23	Enugu	Outcrop	55	441	0.07	0.78
ENU/24	Enugu	Borehole	171	442	0.02	0.80
ENU/25	Enugu	Outcrop	119	438	0.03	0.72
ENU/27	Enugu	Outcrop	68	441	0.12	0.78
		Average	87.29	438	0.06	0.72

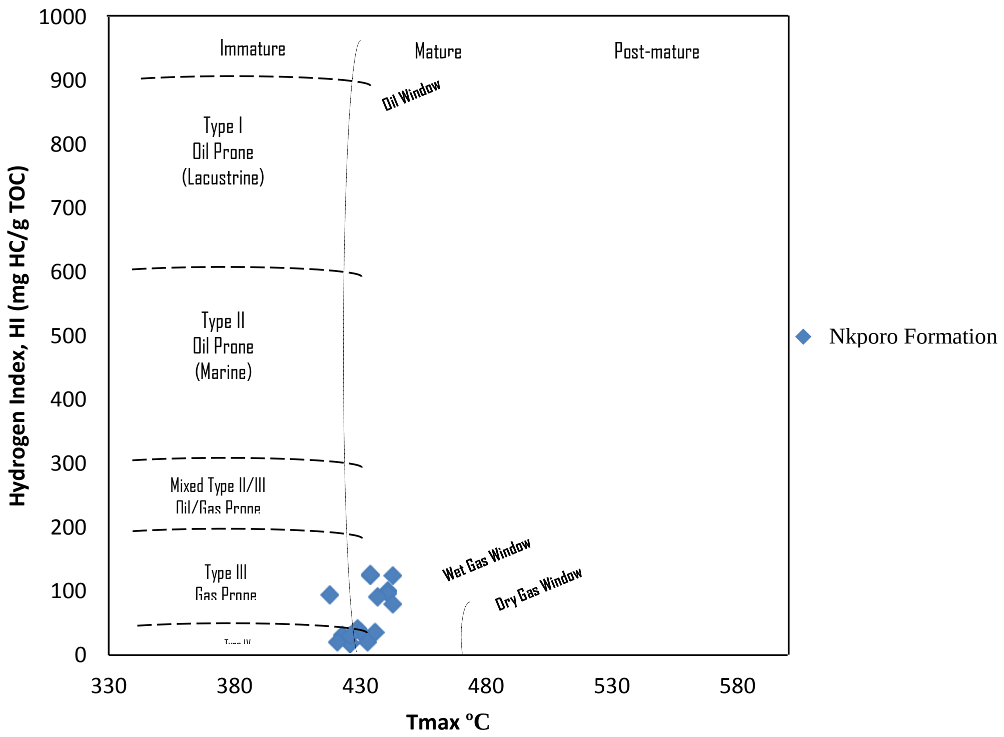

Fig. 4.32a: Plot of Hydrogen Index (HI) versus Tmax of the Nkporo Formation samples (Espitalie et al, 1985)

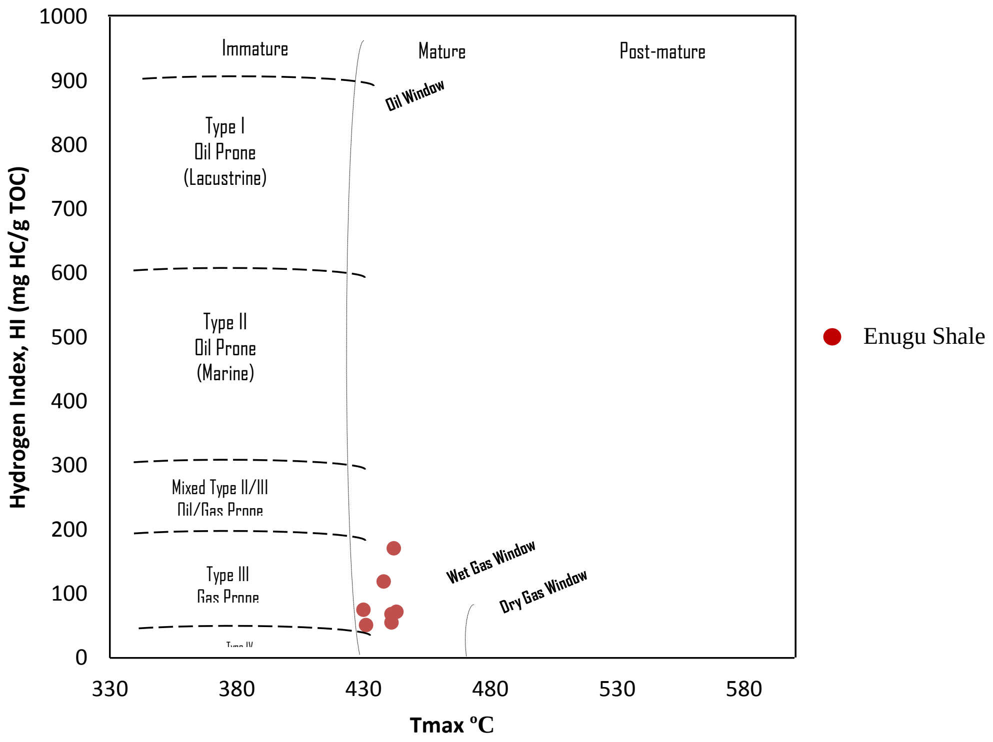

Fig. 4.32b: Plot of Hydrogen Index (HI) versus Tmax of the Enugu Shale samples (Espitalie et al, 1985)

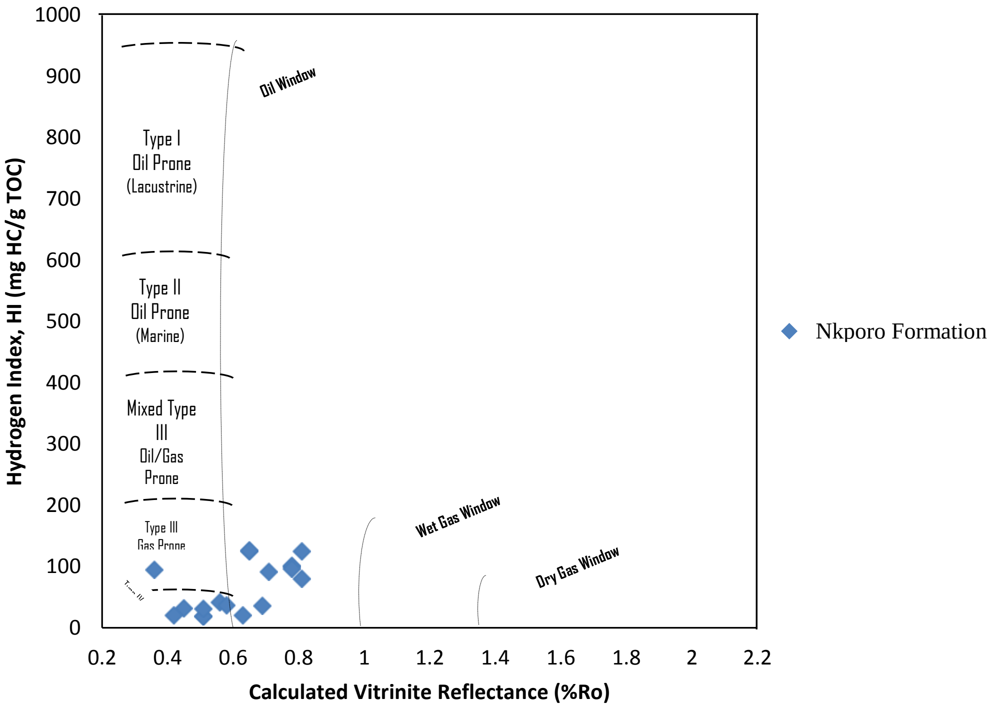

Fig. 4.33a: Plot of Hydrogen Index (HI) versus Calculated Vitrinite Reflectance (%Ro) showing the type and maturity of the Nkporo Formation samples (Espitalie et al, 1985)

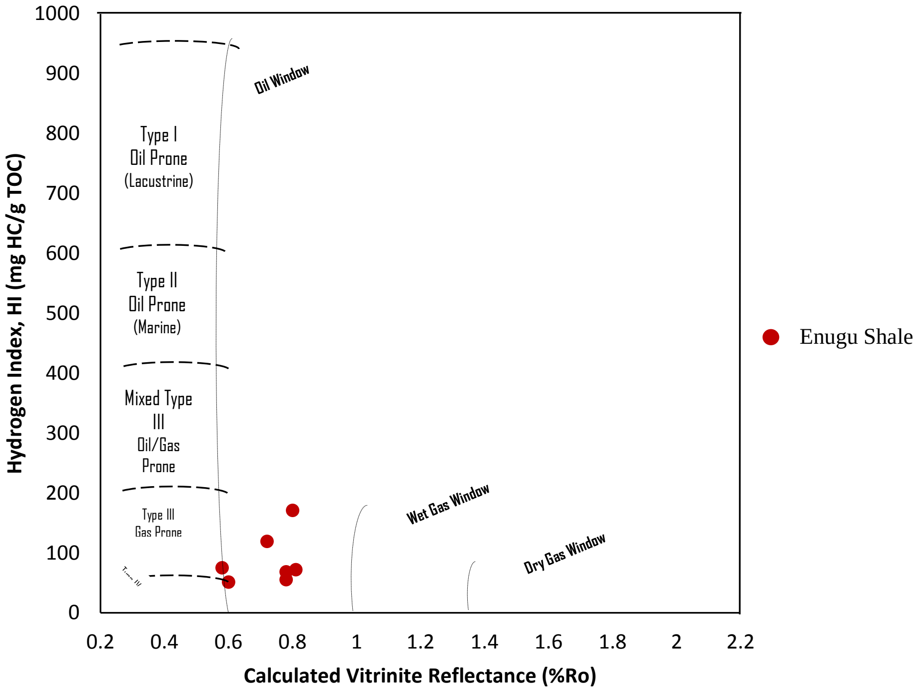

Fig. 4.33b: Plot of Hydrogen Index (HI) versus Calculated Vitrinite Reflectance (%Ro) showing the type and maturity of the Enugu Shale samples (Espitalie et al, 1985)

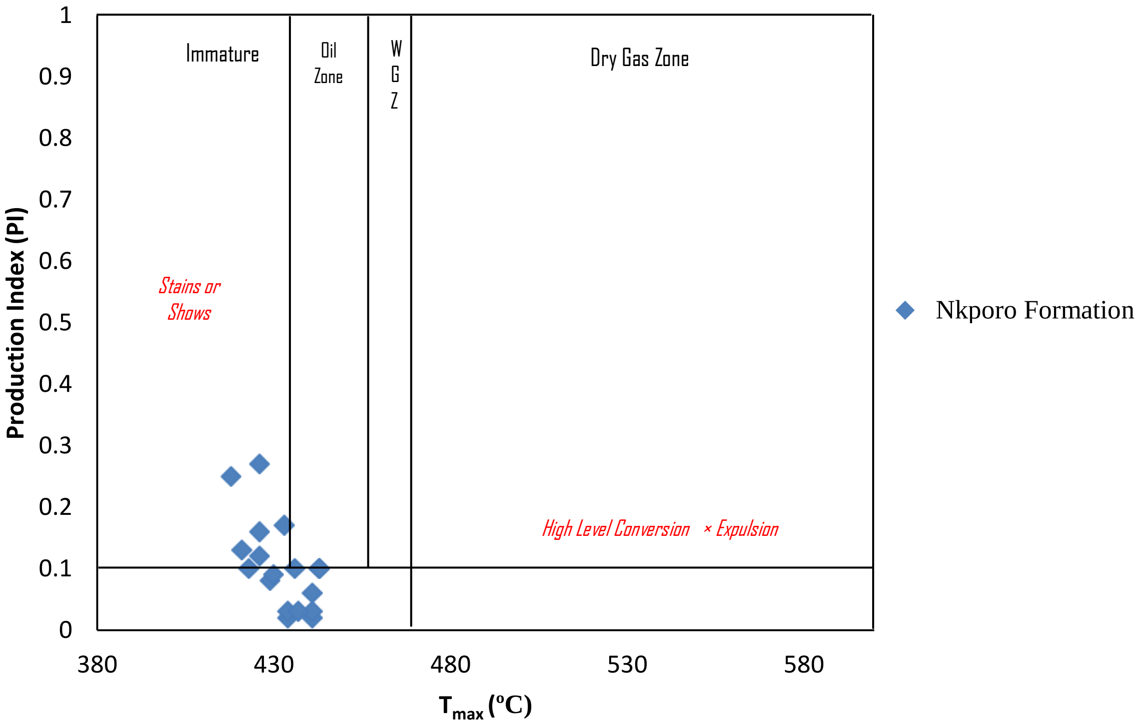

Fig. 4.34a: Plot of Production Index (PI) versus Tmax (°C) showing the type and maturity of the Nkporo Formation samples (Peters, 1986)

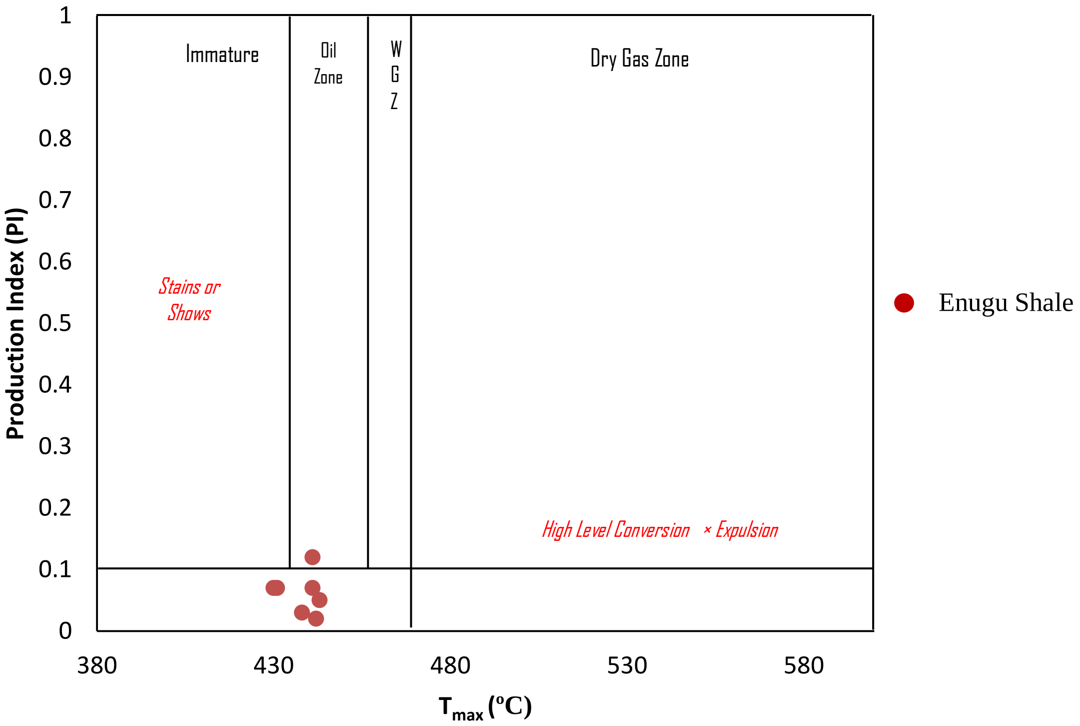

Fig. 4.34b: Plot of Production Index (PI) versus Tmax (°C) showing the type and maturity of the Enugu Shale samples (Peters, 1986)

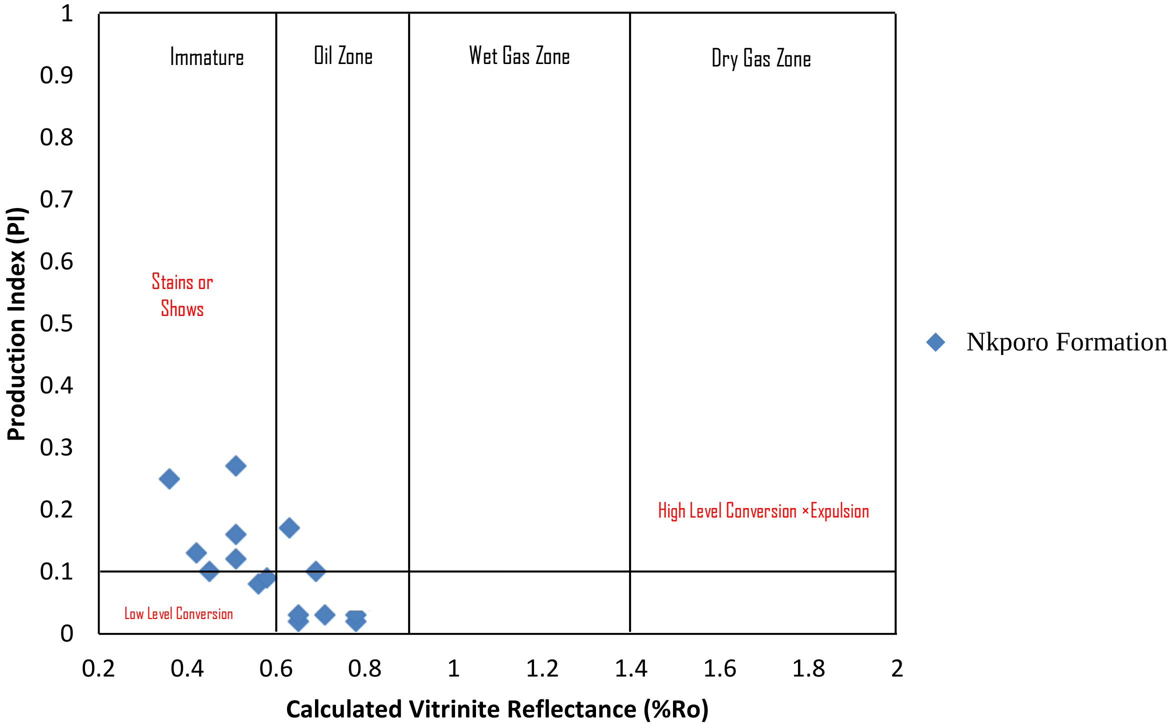

Fig. 4.35a: Plot of Production Index (PI) versus calculated Vitrinite Reflectance (%Ro) showing the maturity of the Nkporo Formation samples (Peters, 1986)

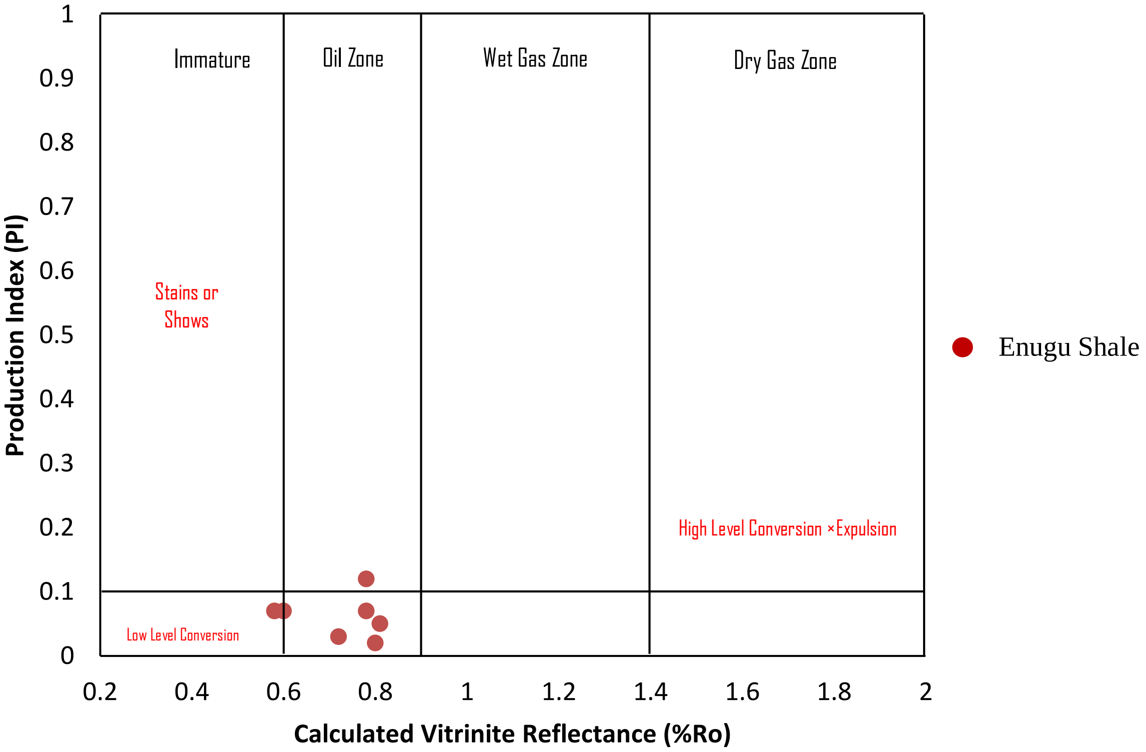

Fig. 4.35b: Plot of Production Index (PI) versus calculated Vitrinite Reflectance (%Ro) showing the maturity of the Enugu Shale samples (Peters, 1986)

The average value of Tmax for Nkporo Formation is 432.33ºC which indicates an immature stage for thermal maturity for oil (Table 4.5a), while that of Enugu Shale has an average value of 438 ºC which indicates an early mature stage for thermal maturity for oil (Table 4.5b). The average value of Production Index, PI, for Nkporo Formation is 0.10 which indicates an early maturity stage for oil, while that of Enugu Shale has an average value of 0.06 which indicates an immature stage for thermal maturity for oil.

The cross-plot of Tmax and Calculated Vitrinite Reflectance (%Ro**)** can be used to further understand the thermal maturity of the source rock (Fig. 4.36a and b). This figure shows a positive correlation between both indices, and indicates mostly thermally mature source rock except seven shale samples which indicate thermally immature source rock in Nkporo Formation, while that of Enugu Shale indicates thermally mature source rocks.

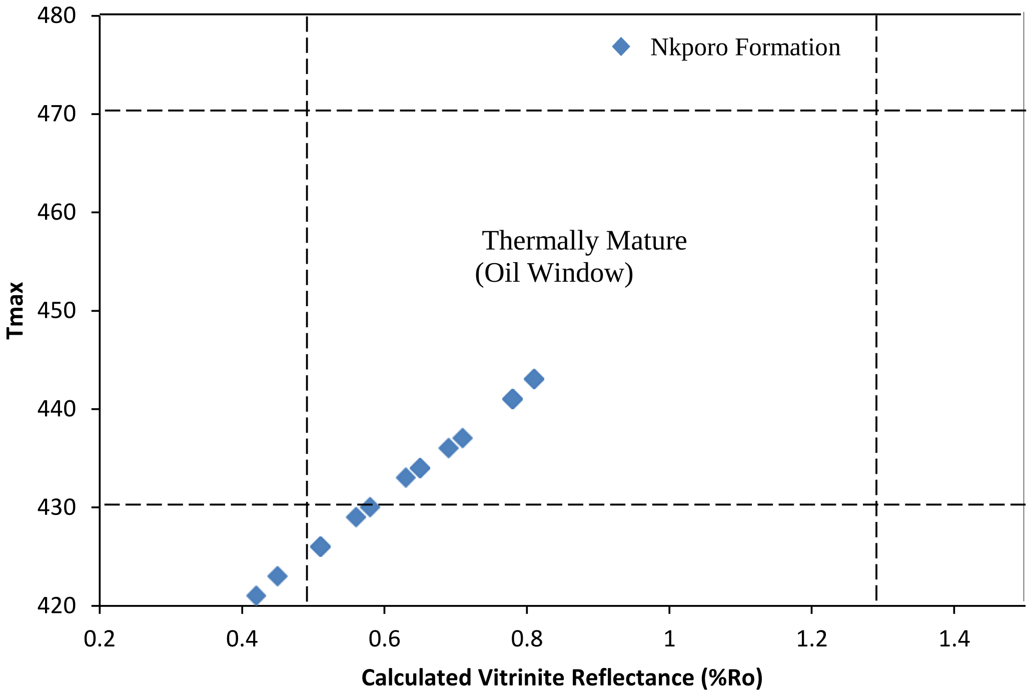

Fig. 4.36a: Plot of Tmax versus Calculated Vitrinite Reflectance (%Ro) to indicate source rock thermal maturity of Nkporo Formation samples (Qadri *et al.* 2016)

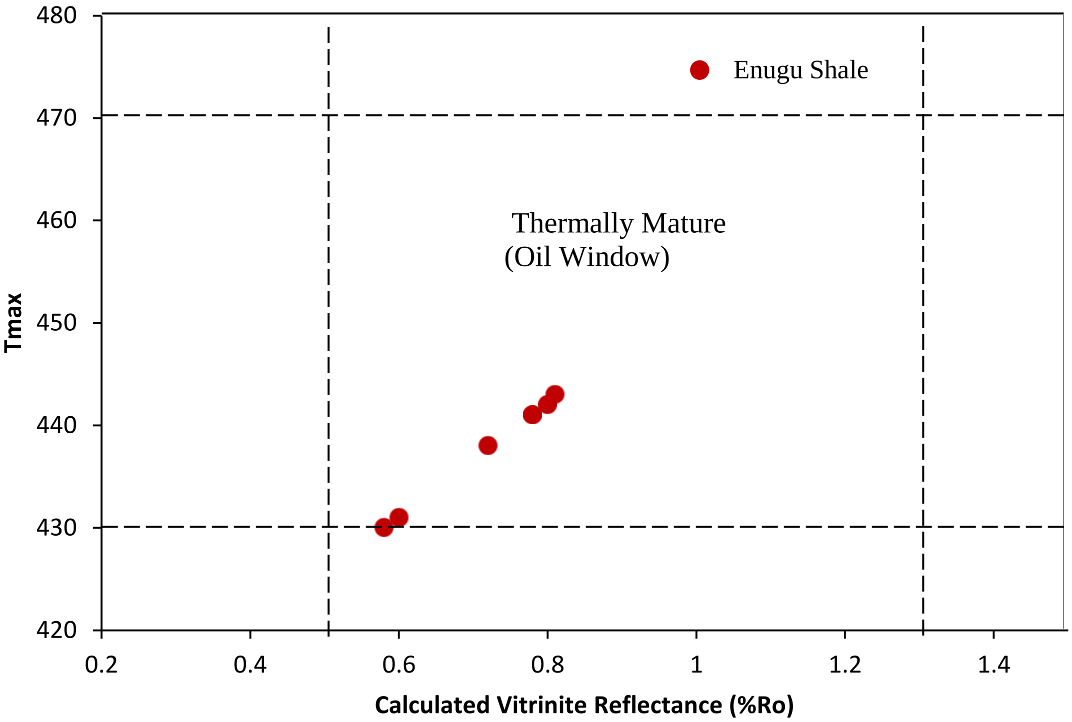

Fig. 4.36b: Plot of Tmax versus Calculated Vitrinite Reflectance (%Ro) to indicate source rock thermal maturity of Enugu Shale samples (Qadri *et al.* 2016)

The summary of the interpreted result of HAWK pyrolysis on shale samples of the Campanian Nkporo Group shows that the Total Organic Carbon (TOC) content of Nkporo Shale ranges from poor to very good source rock which is mostly thermally immature and the percent of maturity is about 33.33%. The Total Organic Carbon (TOC) content of Enugu Shale ranges from fair to very good source rock which is mostly thermally mature and can yield mostly gas and little oil. The percentage maturity of Enugu Shale is about 71.47 (Table 4.6).

The correlation of various maturation indices and zone of petroleum generation and destruction shows that the vitrinite reflectance of Nporo Formation ranges from 0.36 to 0.81 %Ro while that of Enugu Shale ranges from 0.60 to 0.81% (Fig. 4.37a and b). The Tmax of Nkporo Formation ranges from 418 to 441ºC while that of Enugu Shale ranges from 430 to 443ºC. You may recall that the Vitrinite Reflectance and Tmax are indicators in the maturity of organic matter and has a benchmark of 0.60%Ro and 435ºC respectively which reflects the early maturity stage in the generation of hydrocarbon.

Table 4.6: Summary of the Interpreted Result of HAWK Pyrolysis on shale samples of the Nkporo Group

Sample No.	FM	Sample Type	Leco TOC (wt%)	HAWK Tmax (°C)	Calculated %Ro	Hydrogen Index	Generating Potential S1 + S2	Production Index (S1/(S1+S2)	Source Rock	Kerogen Type	Maturity	%Maturity	Hydrocarbon yield
NKP/01	Nkporo	Outcrop	1.24	436	0.69	35	0.49	0.10	Good	IV	Immature	33.33	Gas
NKP/02	Nkporo	Outcrop	0.41	418	0.36	94	0.51	0.25	Poor	III	Immature		Gas Potential
NKP/03	Nkporo	Outcrop	3.54	434	0.65	124	4.5	0.02	V. good	III	Immature		Oil
NKP/04	Nkporo	Outcrop	1.69	429	0.56	41	0.75	0.08	Good	IV	Immature		Gas Potential
NKP/06	Nkporo	Outcrop	1.43	430	0.58	36	0.56	0.09	Good	IV	Immature		Gas Potential
NKP/07	Nkporo	Outcrop	2.42	434	0.65	126	3.16	0.03	V. good	III	Immature		Oil
NKP/08	Nkporo	Outcrop	1.64	441	0.78	99	1.67	0.02	Good	III	Mature		Gas
NKP/09	Nkporo	Outcrop	1.48	426	0.51	18	0.32	0.16	Good	IV	Immature		Gas Potential
NKP/10	Nkporo	Outcrop	0.44	426	0.51	18	0.11	0.27	Poor	IV	Immature		Gas Potential
NKP/12	Nkporo	Outcrop	2.39	423	0.45	31	0.82	0.10	V. good	IV	Immature		Gas Potential
NKP/13	Nkporo	Outcrop	1.27	426	0.51	30	0.43	0.12	Good	IV	Immature		Gas Potential
NKP/14	Nkporo	Outcrop	1.40	421	0.42	20	0.32	0.13	Good	IV	Immature		Gas Potential
NKP/15	Nkporo	Outcrop	0.51	433	0.63	20	0.12	0.17	Fair	IV	Immature		Gas
NKP/16/002	Nkporo	Outcrop	1.53	441	0.78	101	1.65	0.06	Good	III	Mature		Gas
NKP/16/004	Nkporo	Outcrop	2.04	441	0.78	96	2.02	0.03	V. good	III	Mature		Gas
NKP/16/008	Nkporo	Outcrop	2.13	437	0.71	91	2	0.03	V. good	III	Mature		Gas
NKP/17/001	Nkporo	Outcrop	0.67	443	0.81	79	0.59	0.10	Fair	III	Mature		Gas
NKP/17/003	Nkporo	Outcrop	1.38	443	0.81	124	1.9	0.10	Good	III	Mature		Gas
ENU/20	Enugu	Outcrop	3.39	430	0.58	75	2.72	0.07	V. good	III	Immature	71.43	Oil Potential
ENU/21	Enugu	Outcrop	2.30	431	0.60	51	1.26	0.07	V. good	III	Immature		Gas Potential
ENU/22	Enugu	Outcrop	1.58	443	0.81	72	1.19	0.05	Good	III	Mature		Gas
ENU/23	Enugu	Outcrop	0.95	441	0.78	55	0.56	0.07	Fair	III	Mature		Gas
ENU/24	Enugu	Borehole	2.32	442	0.80	171	4.06	0.02	V. good	III	Mature		Oil
ENU/25	Enugu	Outcrop	3.15	438	0.72	119	3.86	0.03	V. good	III	Mature		Oil
ENU/27	Enugu	Outcrop	0.53	441	0.78	68	0.41	0.12	Fair	III	Mature		Gas

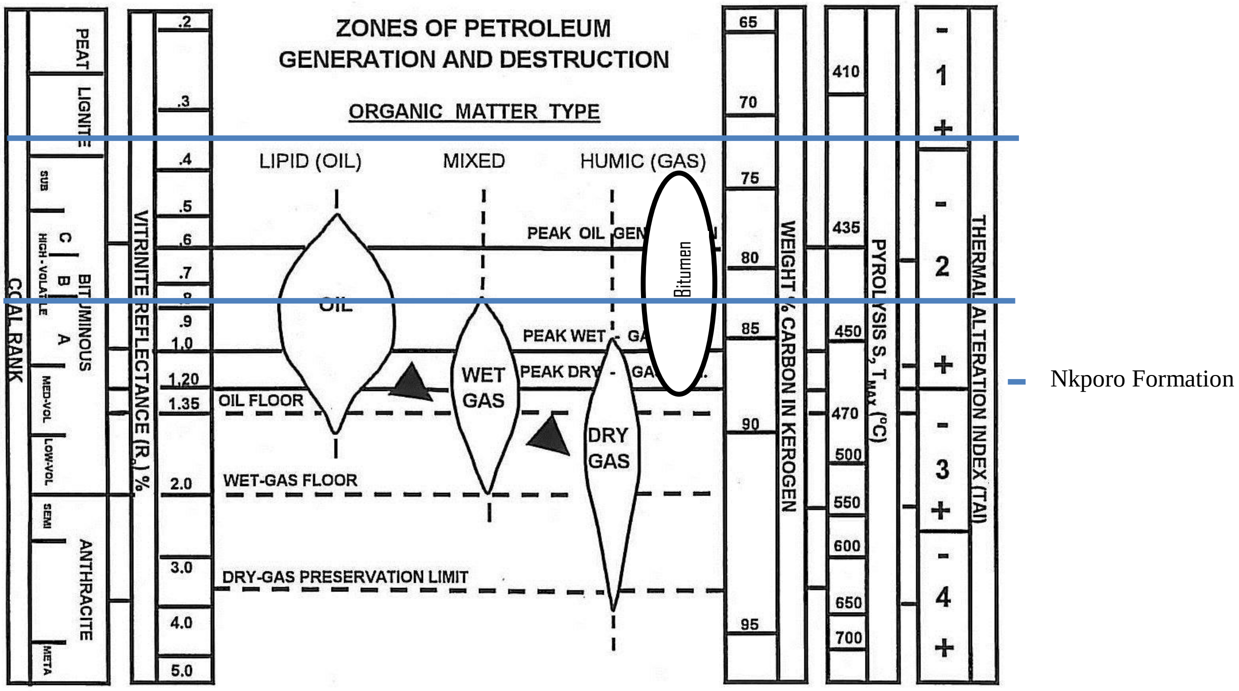

Fig. 4.37a: Correlation of various maturation indices and zone of petroleum generation and destruction of the Nkporo Formation (Javie, 2012)

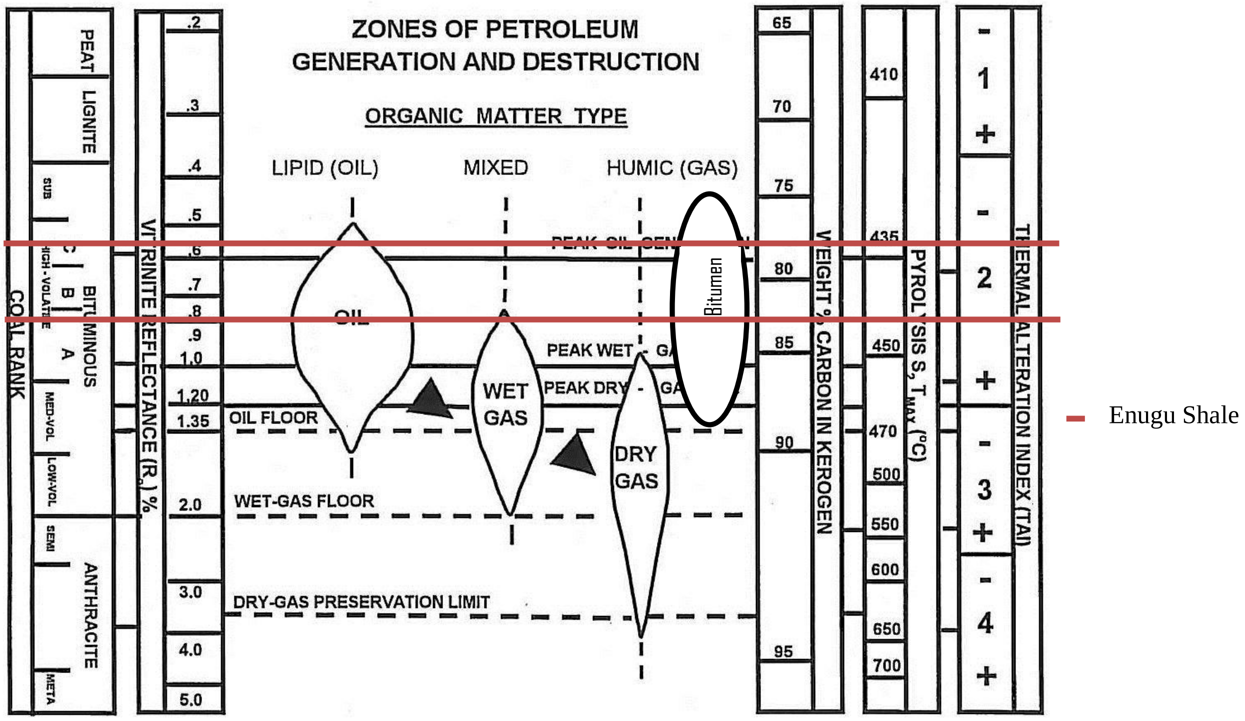

Fig. 4.37b: Correlation of various maturation indices and zone of petroleum generation and destruction of the Enugu Shale (Javie, 2012)

4.4 Visual Kerogen Analysis

From the results of the visual kerogen analysis, The Nkporo Formtion samples has average percent counts of phytoclast of 45%, that of Opaques is about 33.11%, Amorphous Organic Matter (AOM) is about 14.08% and Palynomorphs is about 7.06% (Table 4.7a). This is confirmed by the histogram and area plots showing the abundance of various classes of visual kerogen of Nkporo Formation samples (Figs. 4.38a and 4.39a). The highest number of percent counts produced is the phytoclast having the value of 45% which indicates Type III kerogen (Gas Prone).

The Enugu Shale samples has average percent counts of phytoclast of 35.50%, that of Opaques is about 35.35%, Amorphous Organic Matter (AOM) is about 22.14% and Palynomorphs is about 7.14% (Table 4.7b). This is confirmed by the histogram and area plots showing the abundance of various classes of visual kerogen in Enugu Shale sample (Figs.4.38b and 4.39b). The percentage counts between the phytoclast and Amorphous Organic Matter (AOM) are the same which indicate Oil/Gas Prone. Figure 4.40 shows the photomicrographs of the kerogen slides of the various particulate organic matters (POM) of Nkporo Formation and Enugu Shale. The results of the visual kerogen done for Nkporo Formaton and Enugu Shale show that the source rock is of Type III kerogen which is gas prone and also Type II/III which is Oil/Gas prone respectively (Table 4.8).

Table 4.7a: Results of Visual Kerogen Analysis showing the percent counts of Phytoclast, AOM, Opaques and Palynomorphs of Nkporo Formtion Samples

SAMPLE NO.	PHYTOCLAST (%)	AOM (%)	OPAQUES (%)	PALYNOMORPHS (%)
NKP/01/001	35	15	40	10
NKP/03/002	60	10	25	5
NKP/04/001	55	15	22.5	7.5
NKP/LST/05/002	28	22	45.5	4.5
NKP/06/001	62.5	7	20	10.5
NKP/07/002	57	12	22	9
NKP/08/001	65	10	20	5
NKP/09/002	60	5	20	15
NKP/10/001	40	5	50	5
NKP/12/001	45	30	20	5
NKP/13/001	40	30	25	5
NKP/14/002	50	10	35	5
NKP/15/001	40.5	8.5	45	6
NKP/16/002	25.5	25	45	4.5
NKP/16/004	35	20	40	5
NKP/16/008	40	15.5	35.5	9
NKP/17/001	35	8.5	50.5	6
NKP/17/003	30	5	55	10
Average	**45**	**14.08**	**33.11**	**7.06**

Table 4.7b: Results of Visual Kerogen Analysis showing the percent counts of Phytoclast, AOM, Opaques and Palynomorphs of Enugu Shale Samples

SAMPLE NO.	PHYTOCLAST (%)	AOM (%)	OPAQUES (%)	PALYNOMORPHS (%)
ENU/20/001	45	15	25	15
ENU/21/003	55	10	25.5	9.5
ENU/22/001	60	5	30	5
ENU/23/001	15	50	30	5
ENU/24/001	18.5	40	35	7.5
ENU/25/001	30	25	42	3
ENU/27/001	25	10	60	5
Average	**35.50**	**22.14**	**35.35**	**7.14**

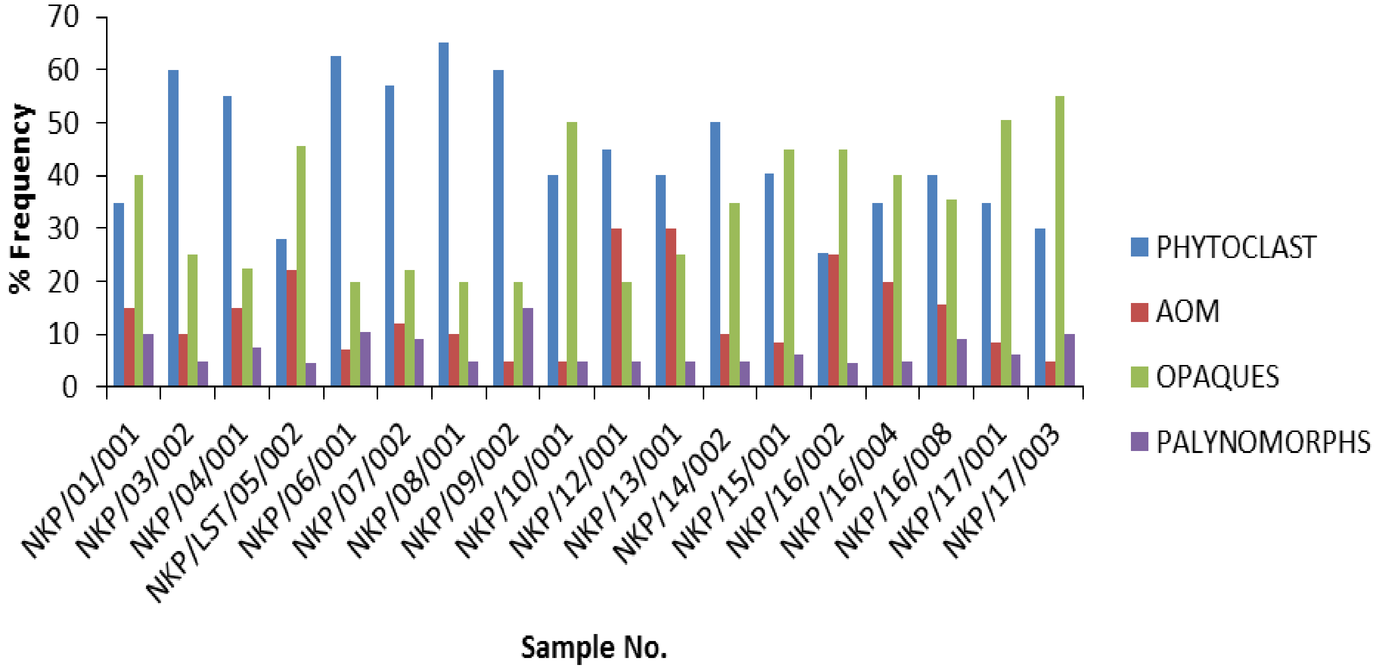

Fig. 4.38a: Histogram showing the comparism of source rock samples and their percent counts between the Phytoclast, AOM, Opaques and Palynomorphs of the Nkporo Formation samples

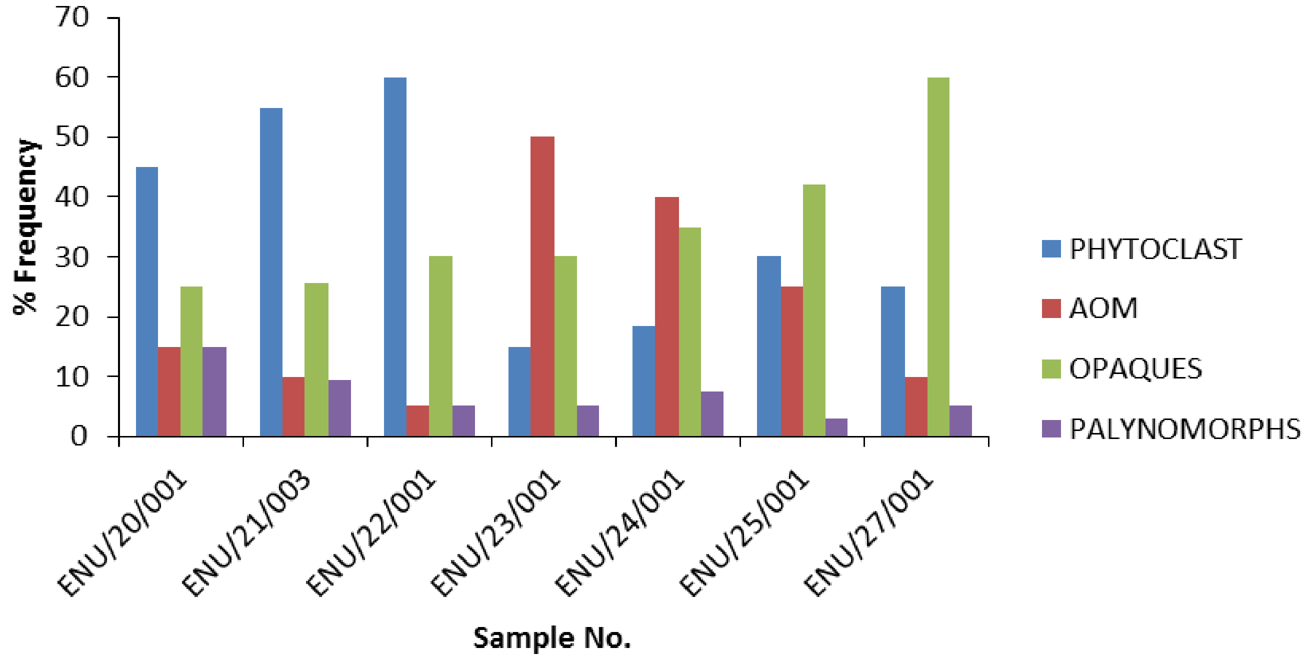

Fig. 4.38b: Histogram showing the comparism of source rock samples and their percent counts between the Phytoclast, AOM, Opaques and Palynomorphs of the Enugu Shale samples

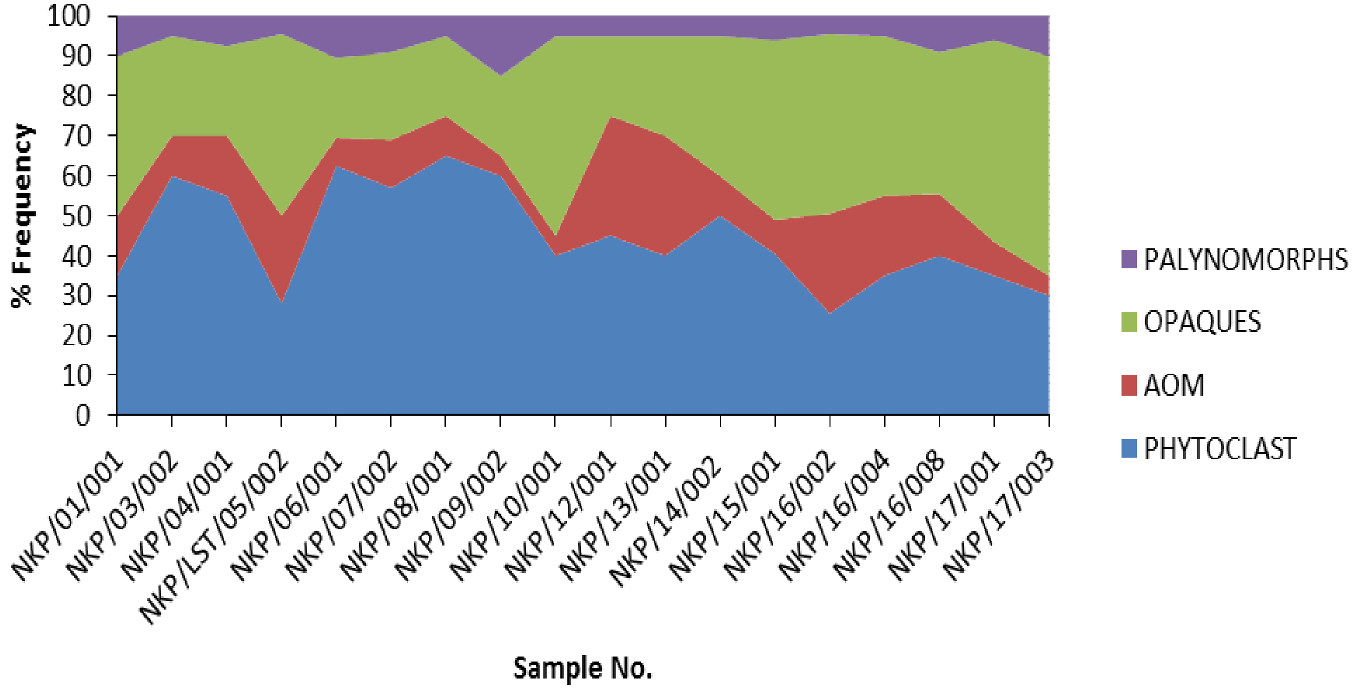

Fig. 4.39a: Area graph showing their percent counts between the Phytoclast, AOM, Opaques and Palynomorphs of the Nkporo Formation samples

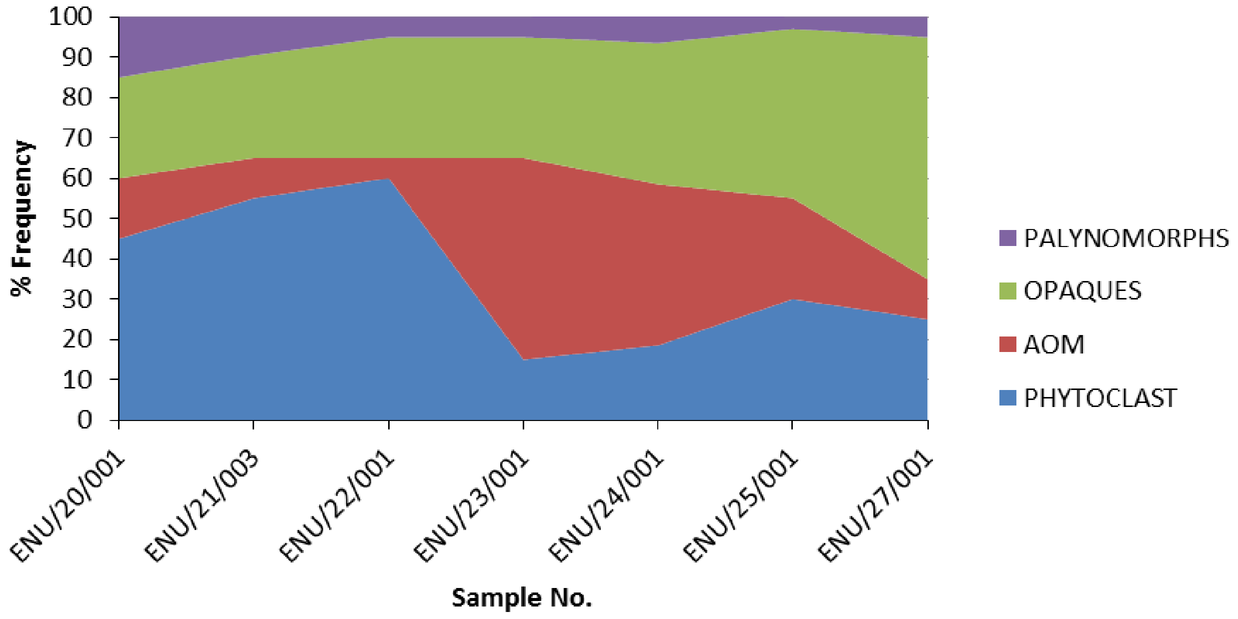

Fig. 4.39b: Area graph showing their percent counts between the Phytoclast, AOM, Opaques and Palynomorphs of the Enugu Shale samples

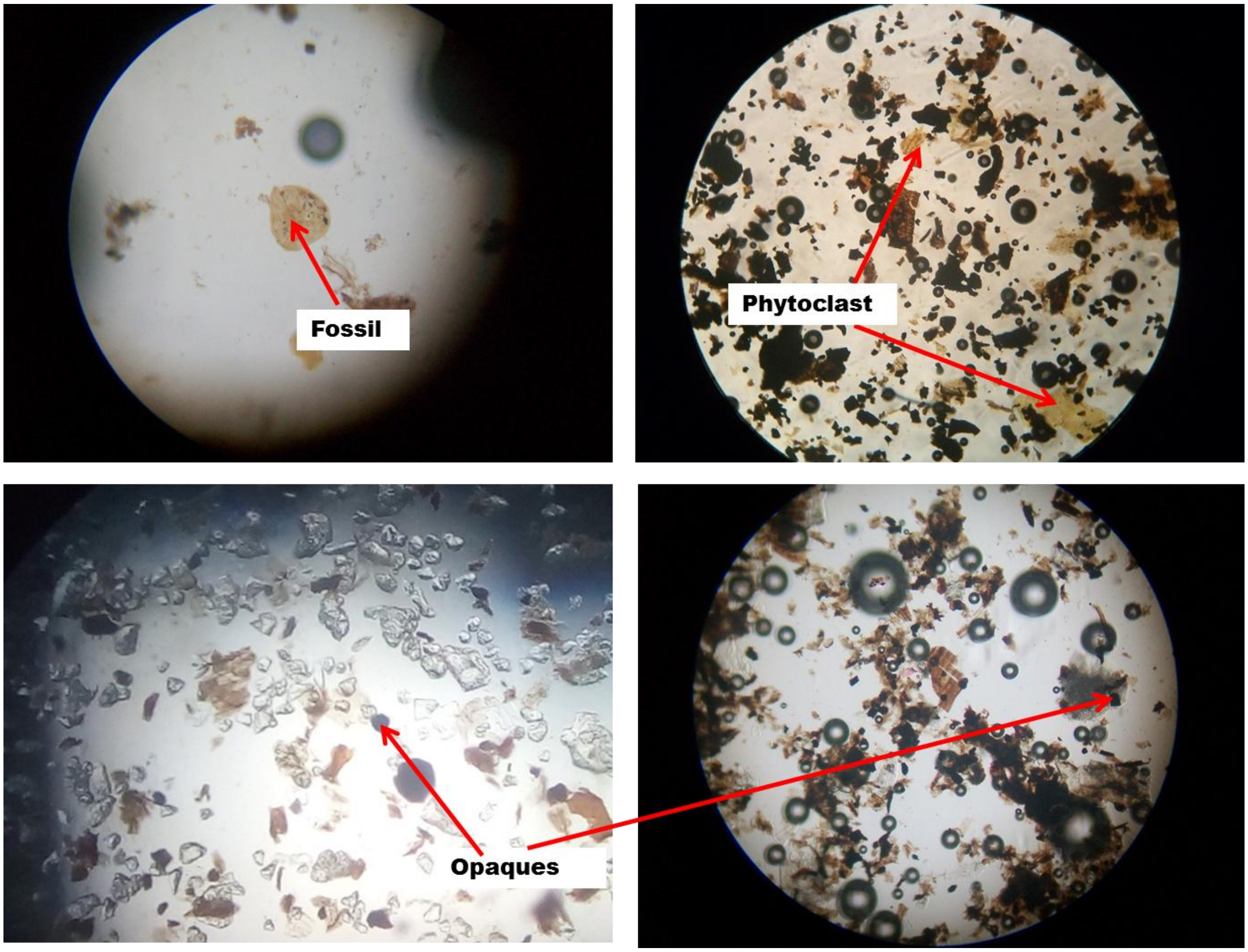

Fig 4.40: Photomicrographs of the kerogen slides showing the various particulate organic matter (POM) of Nkporo Formation and Enugu Shale

Table 4.8: Summary of the Kerogen Optical Assessment and Interpretation of Nkporo Formation and Enugu Shale samples

SAMPLE NO.	PALYNOFACIES ASSOCIATION	S/P COLOUR	THERMAL ALTERATION INDEX (TAI)	VITRINTE REFLECTANCE (Ro %)	THERMAL MATURATION	KEROGEN TYPE	SOURCE ROCK POTENTIAL
NKP/03/002	Mostly phytoclast followed by opaque debris	Colourless to Pale yellow	1 to +1	0.2% to 0.3%	Immature	Type III	Gas Prone
NKP/04/001							
NKP/06/001							
NKP/07/001							
NKP/08/001							
NKP/09/001							
NKP/14/001							
ENU/20/001							
ENU/21/003							
ENU/22/001							
NKP/01/001	Mostly opaque followed by phytoclast debris						
NKP/LST/05/002							
NKP/10/001							
NKP/15/001							
NKP/16/002							
NKP/16/004							
NKP/17/001							
NKP/17/003							
ENU/27/001							
NKP/12/001	Mostly AOM followed by opaque debris					Type II/ III	Oil - Gas Prone
NKP/13/001							
NKP/16/008							
ENU/23/001							
ENU/24/001							
ENU/25/001							

4.5 Biomarker Analysis

The results from the Gas Chromatography- Mass Spectrometry (GC-MS) were calibrated into three major distributions namely n-Alkanes and Isoprenoid, Polycyclic Hydrocarbon (Triterpanes) and Steranes.

4.5.1 Normal Alkanes and Isoprenoid Distribution

The specific geochemical parameters, which have been assessed by the aid of C_{15} analysis, are: Normal alkanes, Isoprenoid (pristane/phytane ratio), isoprenoids/n-alkanes ratio and carbon preference index.

4.5.1.1. Normal Alkanes (n-Alkanes)

It is known that the amorphous sapropelic organic matter is characterized with a maximum peak concentration of C_{14}–C_{25}, reflecting marine organic sources (Waples, 1985). Furthermore, the organic matters which were derived from the remains of higher vascular plants (terrestrial) are characterized by a maximum concentration of n-paraffins at n-C_{25}–C_{29} (Tissot and Welte, 1984).

The n-Alkane in Nkporo and Enugu Formations ranges from C_{14}- C_{35} maximizing at C_{14} and C_{20}. The gas chromatograms of the n-Alkane in Nkporo and Enugu Formations ranges from C_{14}- C_{35} and are characterized by predominance of maximum peak of C_{14}. This pattern of distribution indicates organic matter derived from marine organic sources.

4.5.1.2 Isoprenoid

The most common isoprenoids which are used in this work have a pristane/phytane ratio. The pristane/phytane ratio has been used as an indicator of depositional environment with a low specificity due to the interferences by thermal maturity and source inputs (Peters et al., 2005). The pristane/phytane ratios of oil show some kind of correlation with the canonical variable (CV) values (Sofer, 1984; Chung et al., 1994). They are found that, low pristane/phytane ratio

(<1) and CV (<0.47) associates with carbonate oils, rich in marine organic matter and more than one of pristane/phytane ratio and CV (>0.47) indicates deltaic oils, derived from contribution of terrestrial and detrital sediments.

The pristane/phytane ratios of the Nkporo Formation samples range from 0.33-0.78 while that of Enugu Shale samples range from 0.65-0.75 (Table 4.9). These ratios indicate an anoxic depositional environment rich in marine organic matter (Peters et al., 2005).

4.5.1.3. Isoprenoids/n-Alkanes Ratio

Pristane/n-C_{17} and phytane/n-C_{18} ratios have been used for oil–source rock correlation. These ratios are influenced by the nature of kerogen and extent of generation and maturation (Peters et al., 2005).

The resultant ratios of isoprenoids/n-alkanes (pristane/n-C_{17} and phytane/n-C_{18}) of Nkporo source rocks range from 0.19 to 2.47 and 0.08 to 1.25. While that of Enugu source rocks range from 0.24 to 0.43 and 0.07 to 0.14 (Table 4.9). These ratios reflect that most of the Cretaceous source rocks were derived from mixed organic sources, deposited under transitional environment and show a degree of maturation and no biodegradation (Shanmugum, 1985) (Fig. 4.41a and b). Also the nature of kerogen shows that the Nkporo and Enugu source rocks are of Type II/III kerogen (Fig. 4.42a and b).

Table 4.9: Source and depositional environment parameters computed from *n*-Alkanes and Isoprenoids distributions of Nkporo Formation and Enugu Shale samples

Sample No.	C17	C18	Pr	Ph	Pr/Ph	Pr/nC17	Ph/nC18	CPI	CPI (1)	OEP	OEP (2)
NKP 03	26.857	30.605	27.06	30.605	0.77	0.19	0.08	1.06	0.98	0.48	0.94
NKP 07	26.842	30.304	27.046	30.574	0.55	0.22	0.09	0.84	0.63	0.43	0.73
NKP 08	26.839	30.295	27.035	30.565	0.57	0.34	0.12	1.06	0.87	0.50	0.91
NKP 12	26.835	30.300	27.025	30.596	0.33	2.47	1.25	0.87	0.81	0.87	0.81
NKP 16	26.836	30.296	27.027	30.575	0.78	0.22	0.06	0.85	0.39	0.27	0.60
NKP 17	26.840	30.301	27.032	30.571	0.72	0.25	0.07	0.73	0.58	0.36	0.72
ENU 20	26.832	30.300	27.031	30.572	0.75	0.24	0.07	0.97	0.75	0.44	0.85
ENU 21	26.842	30.299	27.023	30.560	0.65	0.30	0.08	0.98	0.48	0.27	0.72
ENU 24	26.845	30.305	27.113	30.571	0.76	0.43	0.14	1.09	0.91	0.55	0.96
ENU 25	26.846	30.309	27.040	30.584	0.68	0.27	0.11	0.99	0.85	0.50	0.87

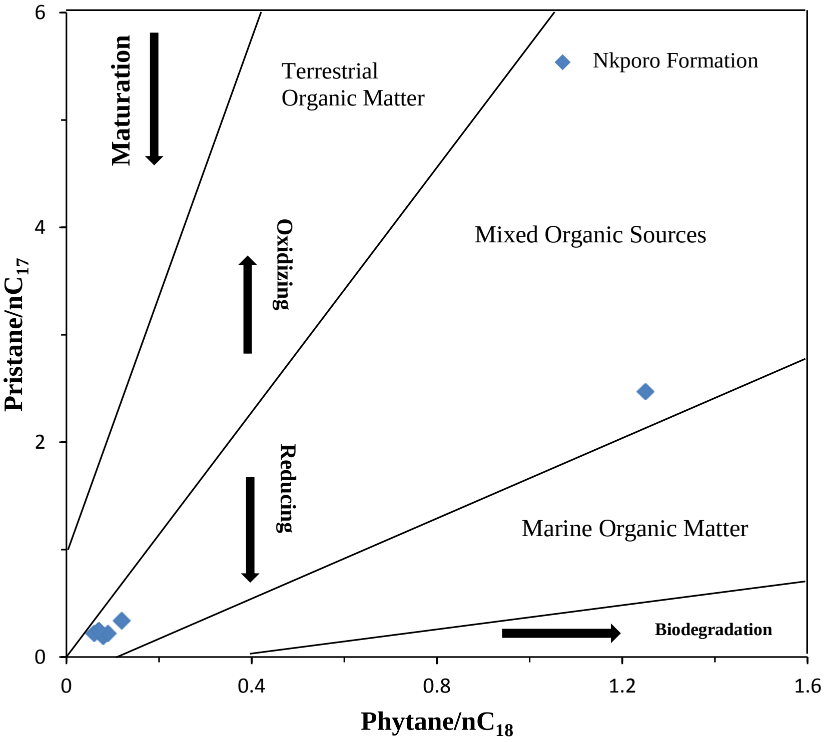

Fig. 4.41a: **Plots of Pr/nC17 against Ph/nC18 of showing the organic sources and maturation of Nkporo Formation samples (Shanmugum, 1985).**

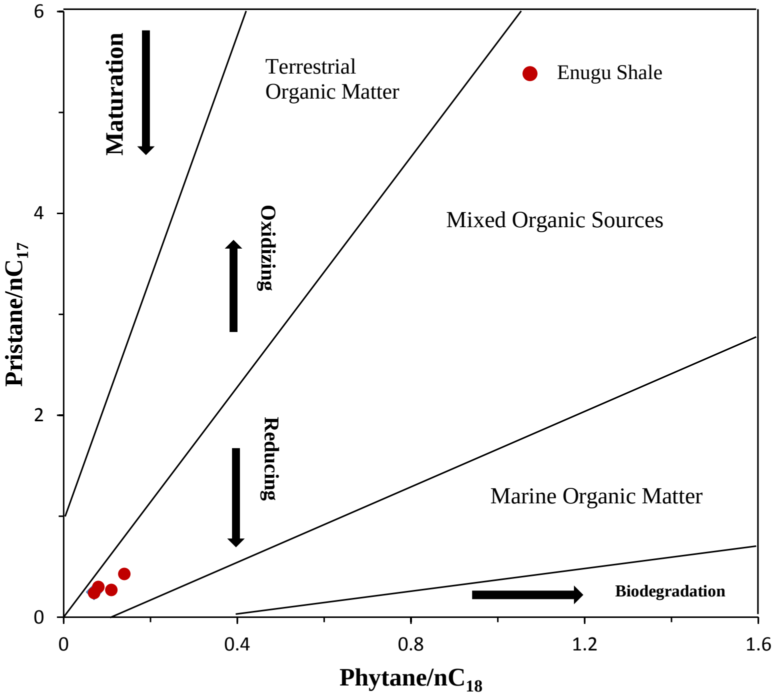

Fig. 4.41b: **Plots of Pr/nC17 against Ph/nC18 of showing the organic sources and maturation of Enugu Shale samples (Shanmugum, 1985).**

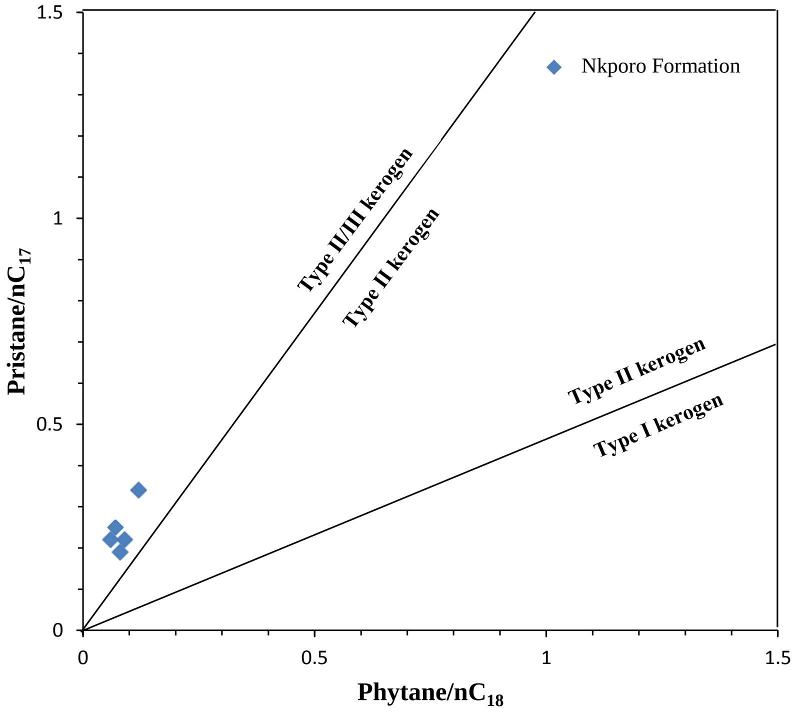

Fig. 4.42a: Plots of Pr/nC17 against Ph/nC18 of showing the type of kerogen of Nkporo Formation samples (Shanmugum, 1985)

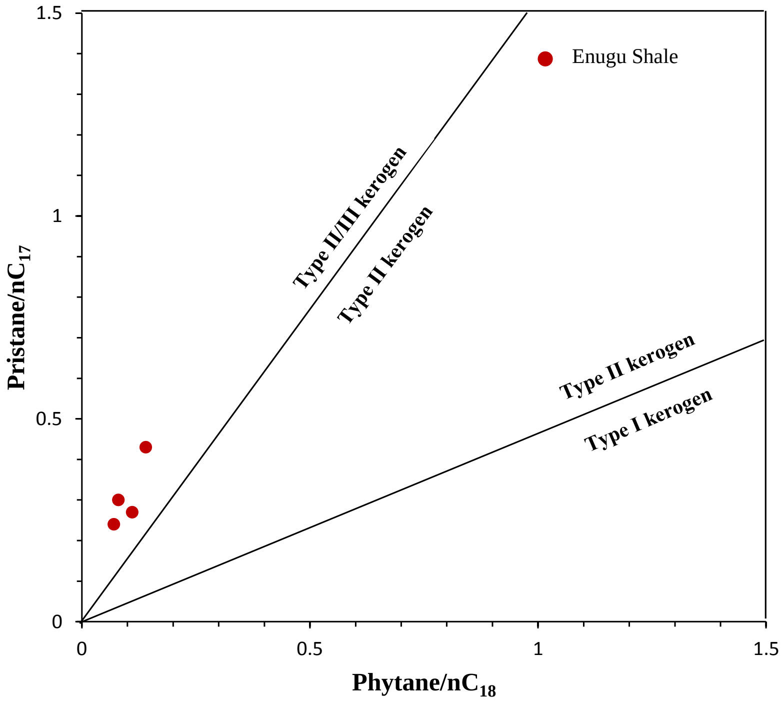

Fig. 4.42b: Plots of Pr/nC17 against Ph/nC18 of showing the type of kerogen of Enugu Shale samples (Shanmugum, 1985).

4.5.1.4. Carbon Preference Index

Carbon Preference Index (CPI) of organic matter is defined as the ratio between the sum of odd-numbered carbon alkanes to the sum of even-numbered carbon alkanes. This parameter gives an indication of the state of a source rock's thermal maturity and the source of the organic matter (Tissot and Welte, 1978). It is thus derived as follows:

CPI = Odd carbon atoms/ Even carbon atoms (Waples, 1985)

The CPI values of the Nkporo Formation range from 0.73 to 1.06 while that of the Enugu Shale range from 0.97 to 1.09 (Table 4.10) indicating that, these source rocks are mainly mature and most probably generated from marine organic sources (Bray and Evans, 1961). Also the plot of CPI against OEP and Pr/Ph against CPI shows that the Nkporo and Enugu source rocks are mature and deposited in a reducing environment respectively (Figs. 4.43a and b) (4.44a and b).

The *m/z* 85 mass chromatograms showing the distribution of *n*-alkane and isoprenoids in the Nkporo samples are shown in Figs.4.45a-f and the Enugu samples is shown in Fig. 4.46a-d.

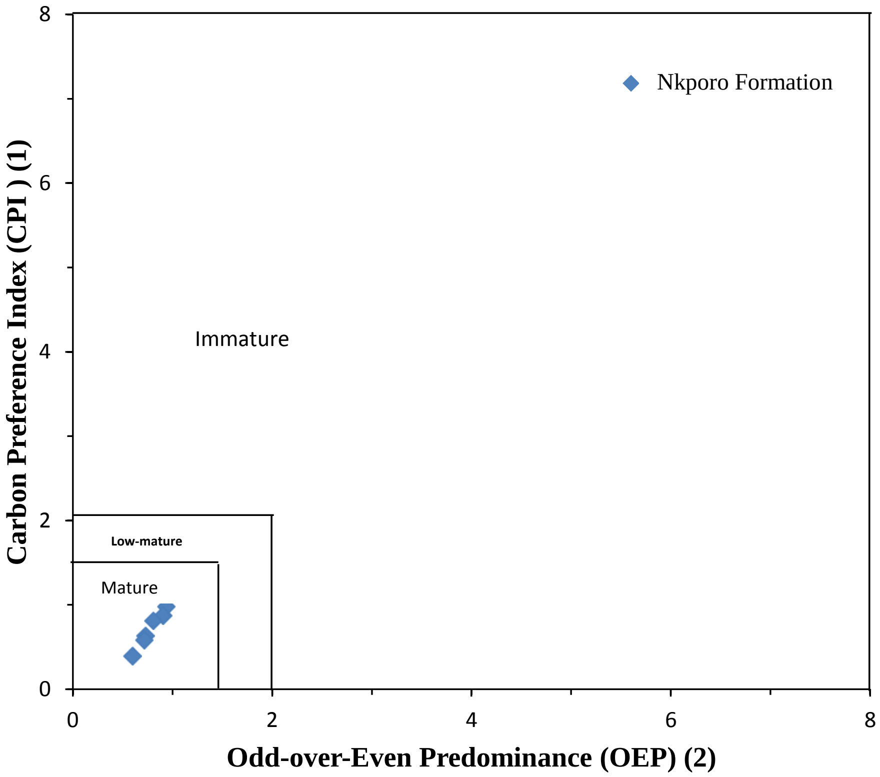

Fig. 4.43a: Plots of CPI against OEP showing the thermal maturity of the Nkporo Formation samples (Bray and Evans, 1961)

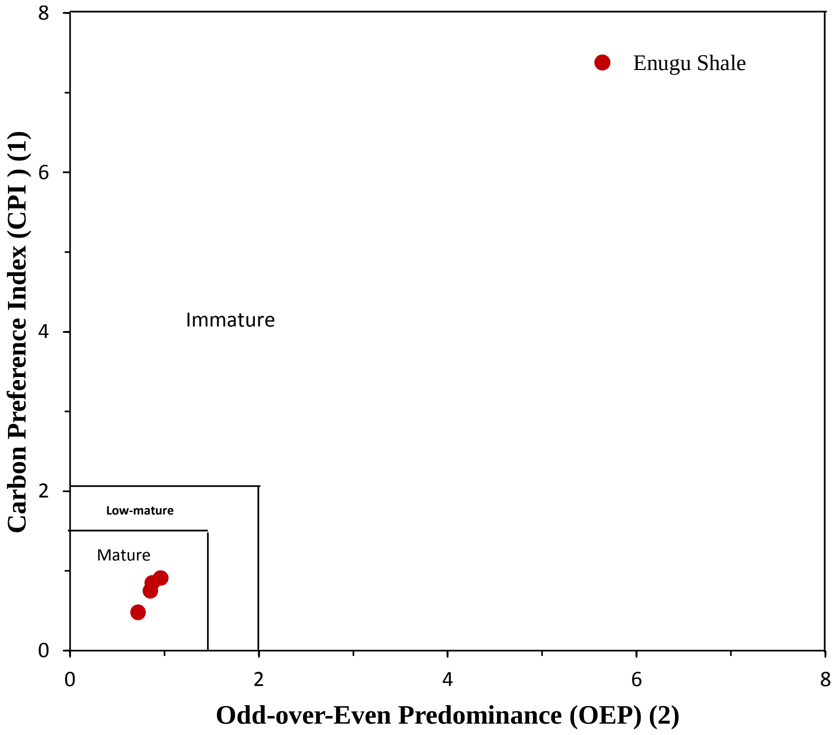

Fig. 4.43b: Plots of CPI against OEP showing the thermal maturity of the Enugu Shale samples (Bray and Evans, 1961)

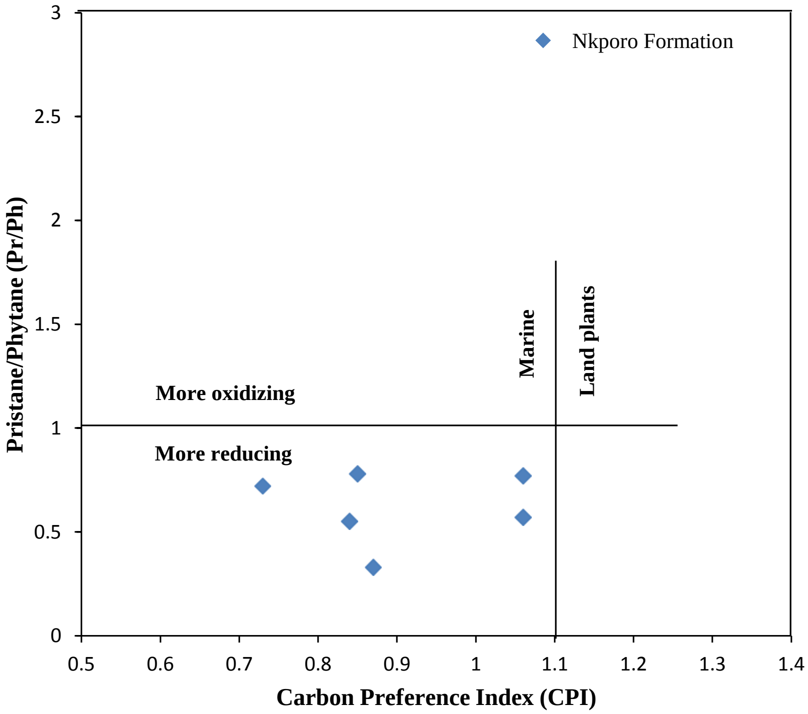

Fig. 4.44a: Plots of Pr/Ph against CPI showing the deposition environment of Nkporo Formation samples (Bray and Evans, 1961)

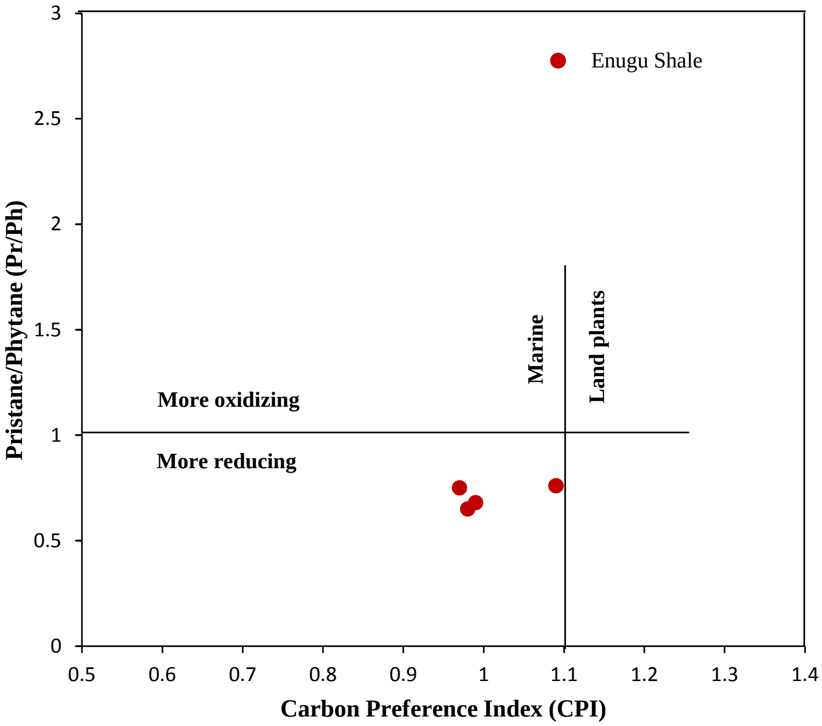

Fig. 4.44a: Plots of Pr/Ph against CPI showing the deposition environment of Enugu Shale samples (Bray and Evans, 1961)

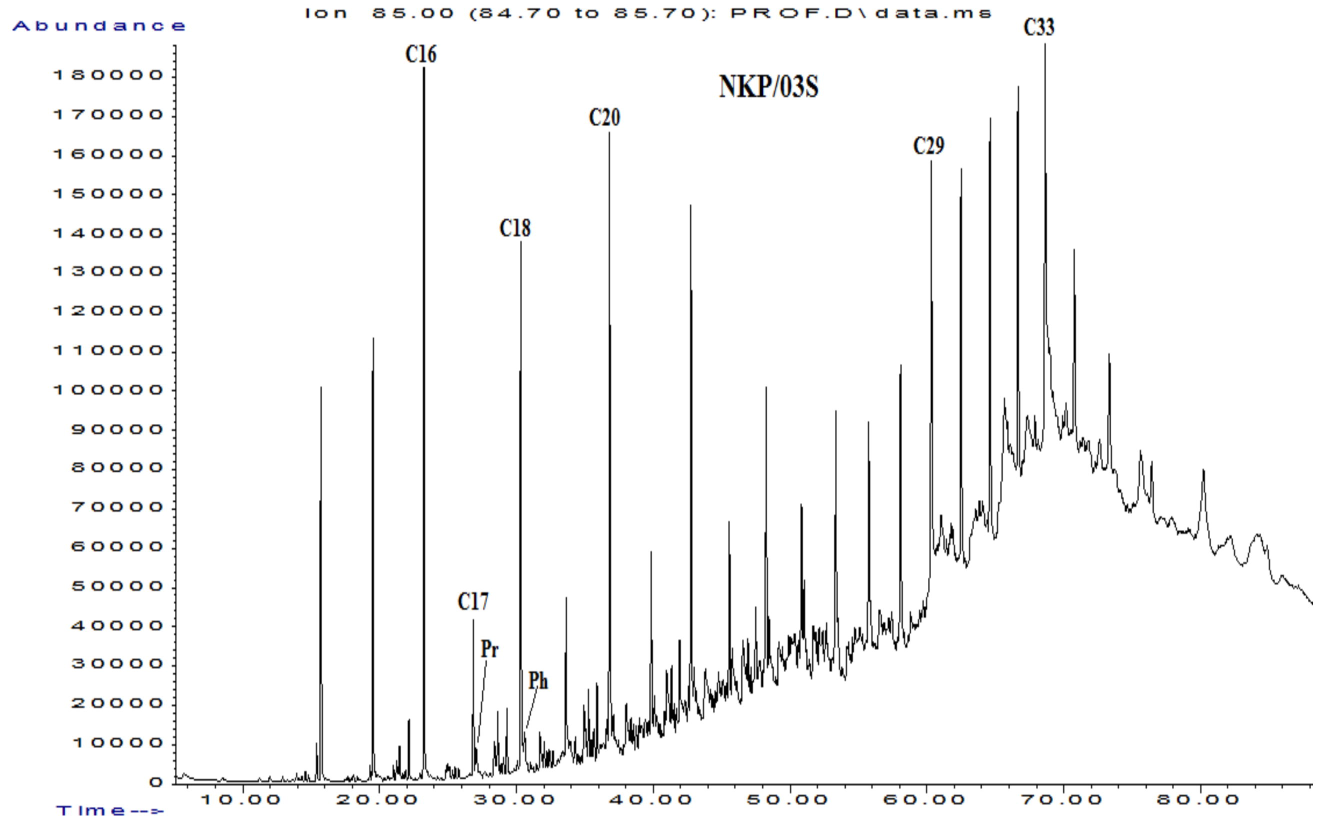

Fig. 4.45a: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/03).

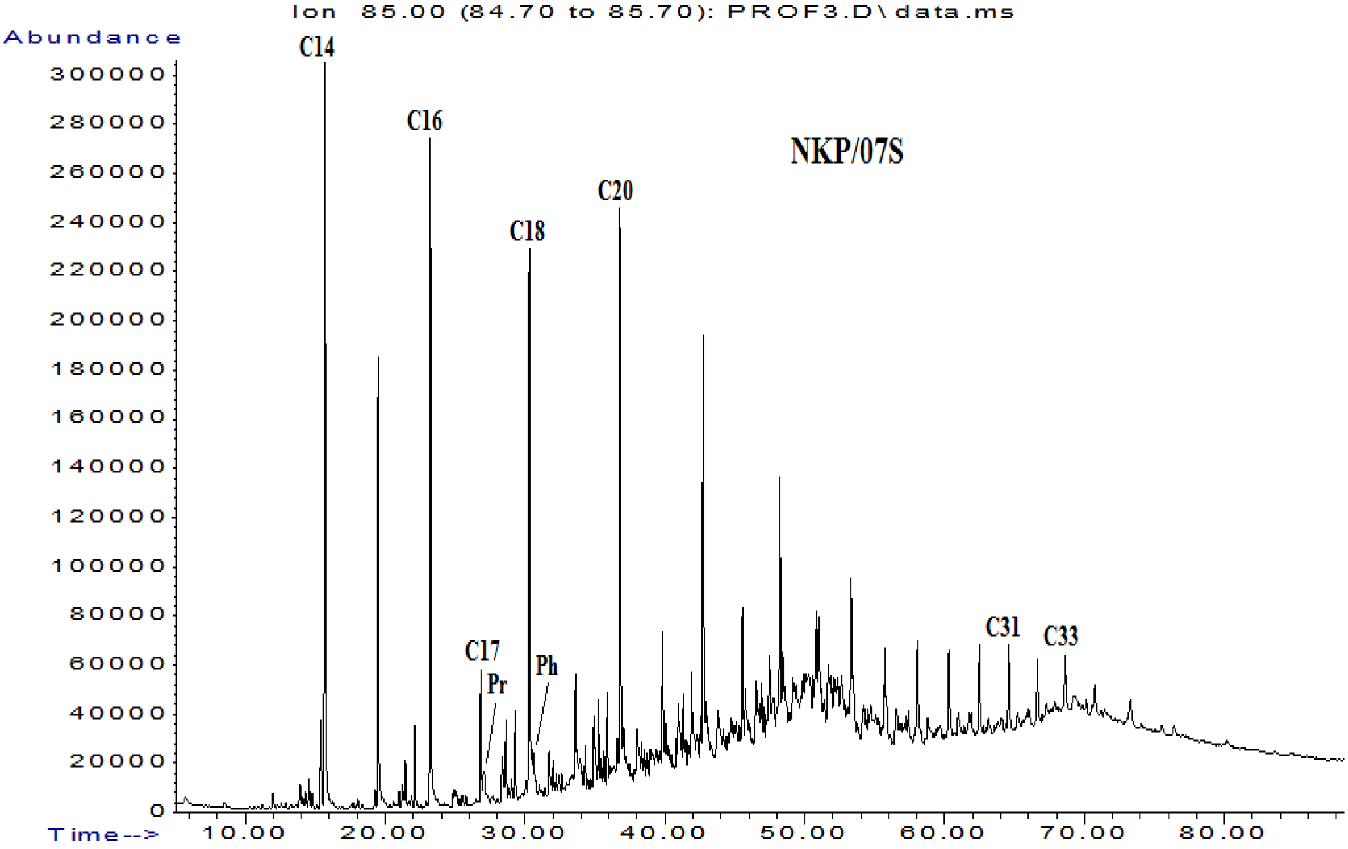

Fig. 4.45b: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/07).

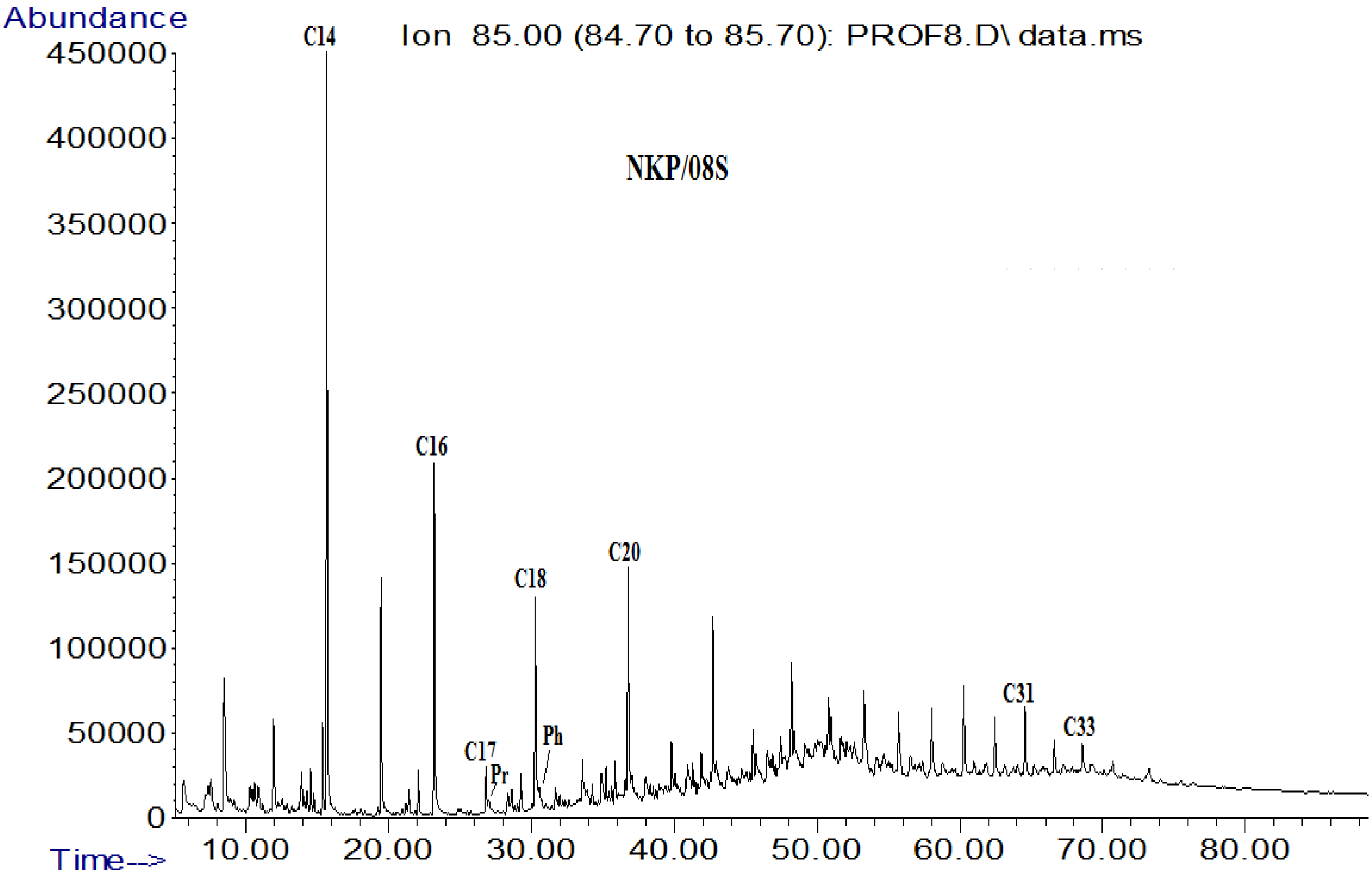

Fig. 4.45c: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/08).

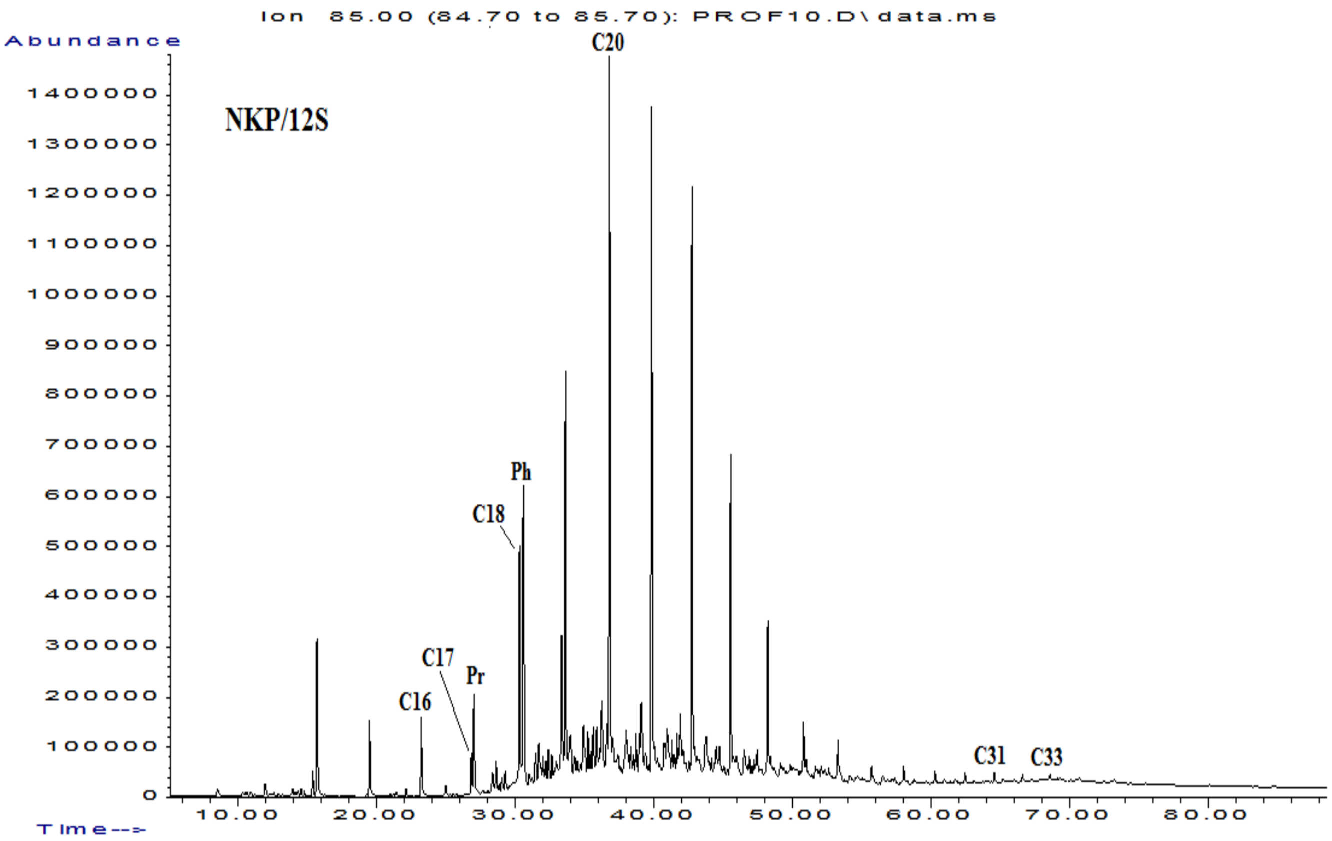

Fig. 4.45d: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/12).

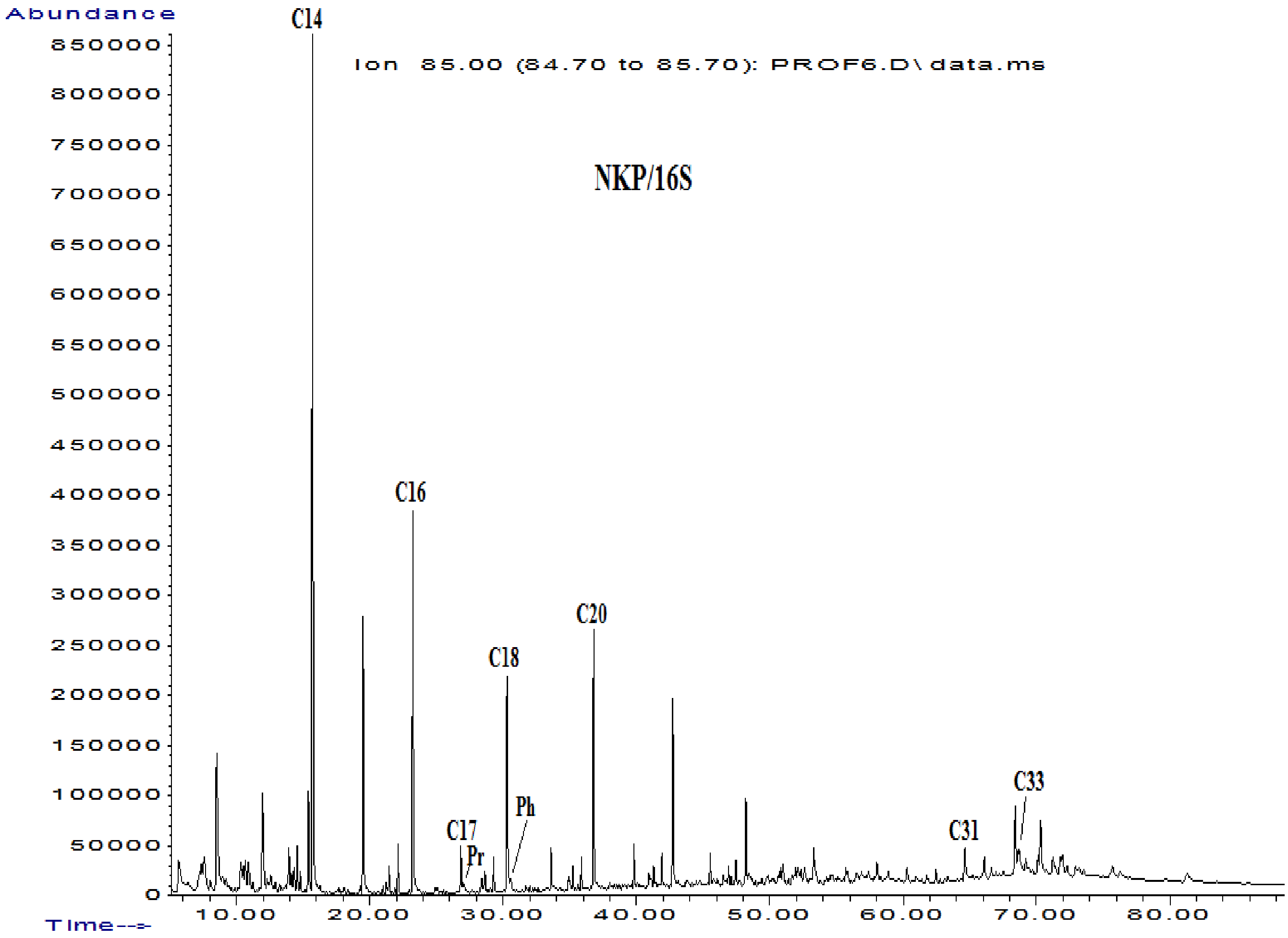

Fig. 4.45e: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/16).

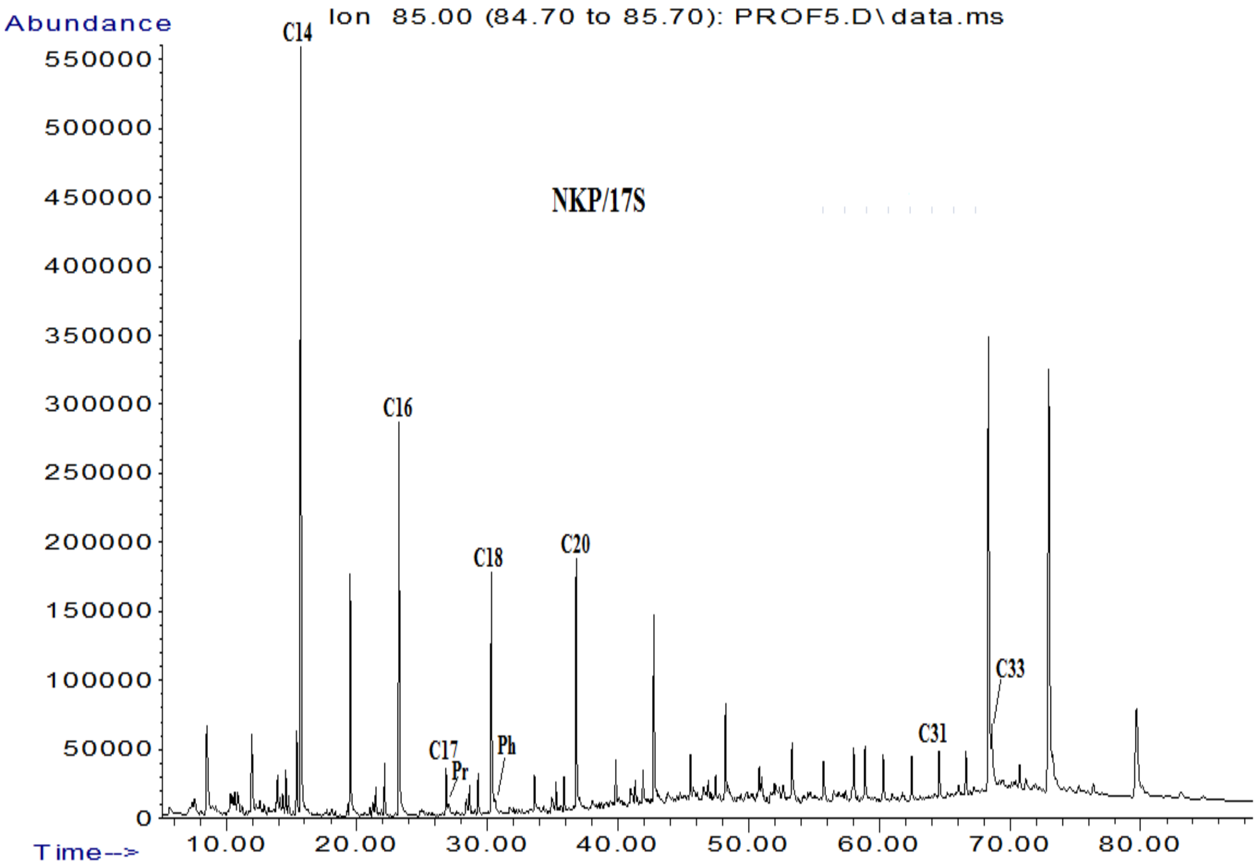

Fig. 4.45f: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Nkporo Formation (NKP/17).

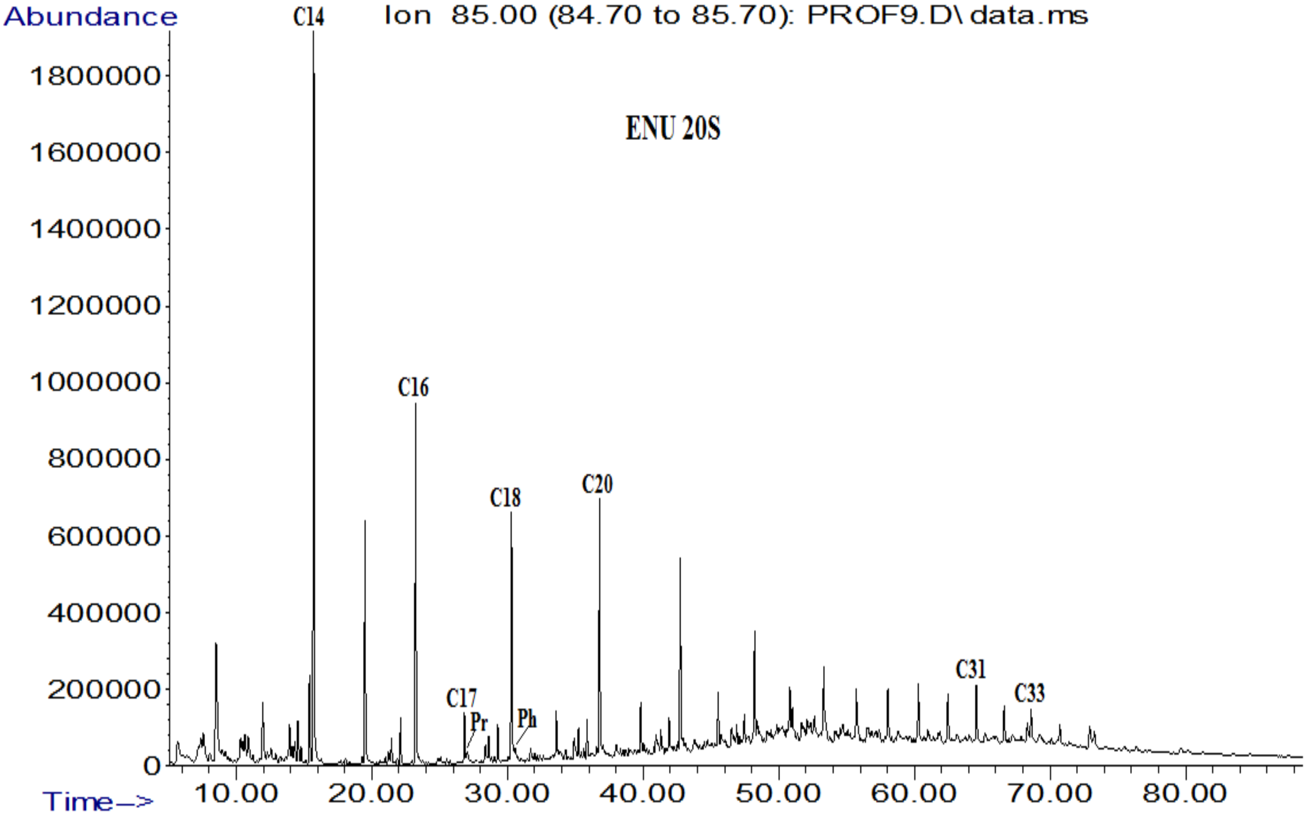

Fig. 4.46a: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/20).

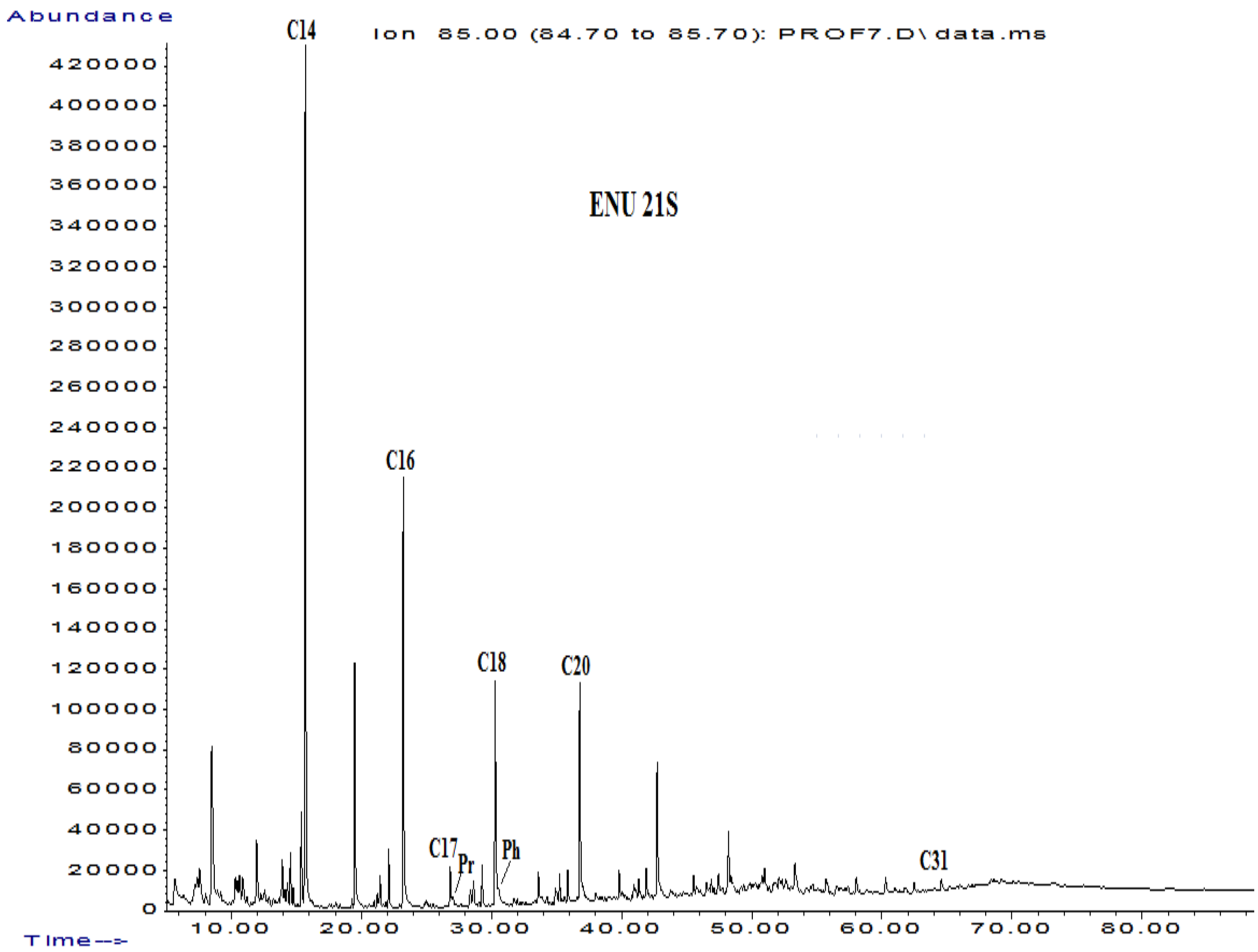

Fig. 4.46b: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/21).

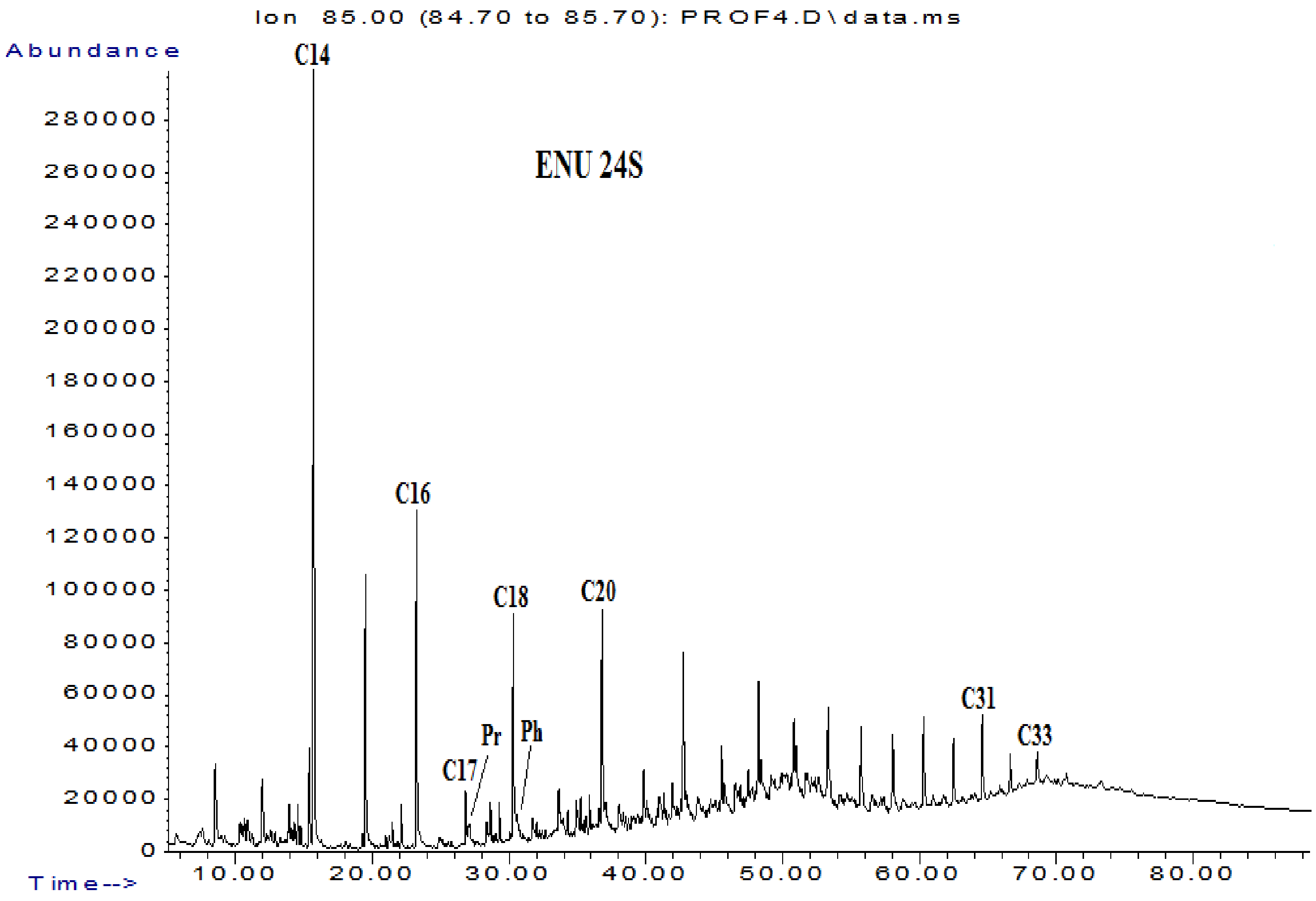

Fig. 4.46c: Gas chromatograms (m/z 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/24).

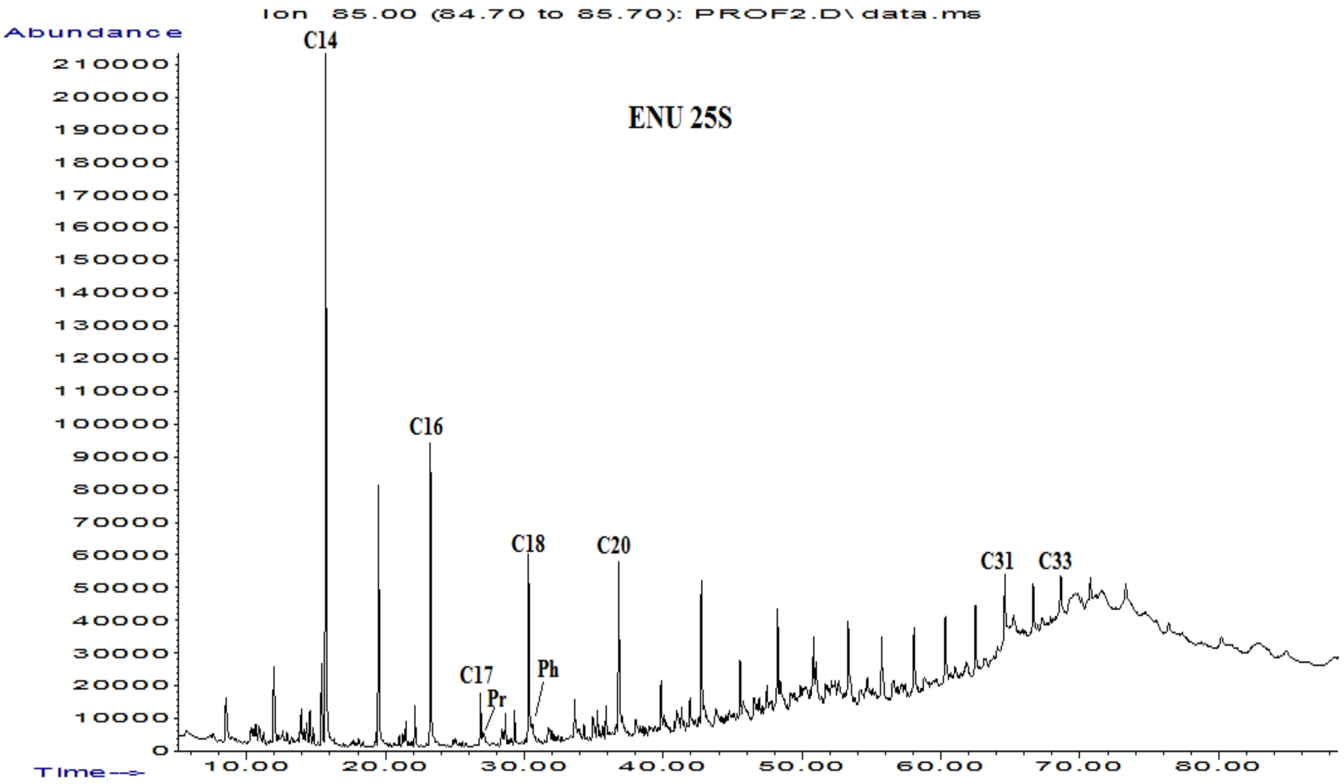

Fig. 4.46d: Gas chromatograms (mz 85) of the saturated hydrocarbon fractions showing the distribution of n-Alkanes of Enugu Shale (ENU/25).

4.5.2 Polycyclic-hydrocarbons

The most common polycyclic biomarker compounds used in this work are tricyclic and tetracyclic terpanes, moretanes, gammacerane, oleanane and pentacyclic extended hopane.

4.5.2.1 Tricyclic and tetracyclic terpanes

A series of tricyclic terpanes ranging from C_{19} to C_{29} were observed in Nkporo Formation and Enugu Shale samples. (Figs. 4.47a-f and 4.48a-d). The source rocks have low percentages of C_{19} to C_{26} tricyclic terpanes which indicate organic matter derived from marine origin. The C_{24}tetra/C_{26}tri(R+S) ratios range between 0.63- 2.0 and 0.55-1.54 for the Nkporo Formation and Nkporo Shale respectively, probably both reflecting marine organic matter input (Table 4.10).

Various ratios of tricyclic terpanes have been used to distinguish marine carbonate, lacustrine, paralic, coal/resin and evaporitic source depositional environments. C_{22}/C_{21} tricyclic terpane ratio in the samples range from 0.25 to 1.47 for the Nkporo Formation and 0.57 to 1.07 for the Enugu Shale, suggesting organic matter were both deposited in fluvial/deltaic to marine depositional environment (Table 4.10). C_{24}tetra/C_{30}hopane ratio has also been used to assess depositional environment of source rocks. C_{24}tetra/C_{30}hopane ratios in the sample range between 0.09 and 0.14 for Nkporo Formation, while that of Enugu Shale is between 0.07 and 0.08. These values also indicate organic matter deposited in fluvial/deltaic-marine depositional environment (Table 4.10).

Table 4.10: Source and depositional environment parameters from tri- and tetracyclic terpanes of Nkporo Formation and Enugu Shale samples

Sample No.	%C19-C21 triterpane	%C23 triterpane	C24tetra/C26(R+S) tri	C24tetra/ C30Hopane	C22/C21 triterpane
NKP/ 03	NIL	NIL	1.56	NIL	0.7
NKP/07	NIL	NIL	1.78	0.09	0.7
NKP/08	NIL	NIL	0.63	0.08	0.55
NKP/12	58.3	41.7	1.08	0.14	0.27
NKP/16	40.7	59.3	1.16	0.11	0.25
NKP/17	NIL	NIL	2	0.11	1.46
ENU/20	25.1	74.9	0.56	0.08	0.6
ENU/21	NIL	NIL	1.19	0.08	0.83
ENU/24	NIL	NIL	1.54	0.07	1.07
ENU/25	NIL	NIL	0.55	0.08	0.57

C24tetra/C30hopane = C24tetracyclic terpane/C30hopane

C24tetra/C26(R+S)tri = C24tetracyclic terpane/C26(R+S)tricyclic terpane

NKP- Nkporo Formation

ENU- Enugu Shale

4.5.2.2 Moretanes

High moretanes concerntration seemed to be abundant in organic materials of terrestrial origin (Mann et al., 1987). Also very low moretanes concerntration seemed to be abundant in organic materials of marine origin (Figs. 4.47a-f and 4.48a-d) shows that moretanes (peak MOR, see peak identification in Table 4.12) in Nkporo Formation and Enugu Shale having very low concerntrations and slightly abundant, indicating contribution from marine sources (Mann et al., 1987). Moretanes are less stable with an increase in maturity; this is because of their relatively low concentrations in oil samples (Mann *et al.,* 1987).

4.5.2.3 Gammacerane

High gammacerane concentrations were originally considered to be markers for lacustrine facies. Gammacerane occurs in major or minor concentrations in many rocks that are definitely not of lacustrine origin as they are dominant in marine rocks (Waples and Machihara 1992). Lacustrine environment has abundant gammacerane and considered also as a salinity marker (Fu Jiamo et al. 1989). Gammacerane (peak G, Figs. 4.47a-f and 4.48a-d, see peak identification in Table 4.12) is only detected, in a relatively low amount, in Nkporo Formation and Enugu Shale indicating input of marine organic matter in different saline environments.

4.5.2.4 Oleanane

Low or absent oleanane concentrations are originally considered to be markers for marine facies (Peters and Moldowan, 1993). Also high oleanane concentrations are originally considered to be markers for terrigenous facies (Peters and Moldowan, 1993). Figures 4.47a-f and 4.48a-d show that oleanane (peak OLE, see peak identification in Table 4.12) of Nkporo Formation and Enugu Shale has very low concerntrations, both indicating contribution from marine sources (Mann *et al.,* 1987). Oleananes are regarded as reliable marker for angiosperm; being significant constituents of wood, roots and bark in Cretaceous or younger effective source rocks in deltaic petroleum system (Moldowan *et al.,* 1994; Nytoft *et al.,* 2002; Peters *et al.,* 2005; Ozcelik and Altunsoy, 2005; Otto *et al.,* 2005; Bechtel *et al.,* 2007b) There are presence of oleananes in both Nkporo Formation and Enugu Shale which indicates that the organic matter were derived from higher land plants of Cretaceous or younger age.

4.5.2.5 Pentacyclic extended hopane

The unusually large amount of C_{35} extended hopane seems to be associated with marine carbonates or evaporites. High C_{35}/C_{34} ratios in marine environment with a low redox potential rather than with lithology as not all carbonate rocks have high C_{35} concentration (Peters and Moldowan, 1991). The concentration of C_{35} extended hopane

(Figs. 32 and 33, see peak identification in Table 4.12) is more abundant in Nkporo Formation and Enugu Shale. These results indicate marine environment.

4.5.3 Hopanes and homohopanes

C_{29}/C_{30} hopanes ratios are generally high (>1) in oils generated from organic rich carbonates and evaporates (Connan *et al.,* 1986). The majority studied source rock samples, having lower concentrations of C_{29} than C_{30} hopane, with low C_{29}/C_{30} hopane ratios range from 0.71 to 0.82 of the Nkporo source rocks and 0.59 to 0.79 of Enugu source rocks (Table 4.11), These data illustrate that the shale samples might be sourced from source rocks rich in carbonaceous organic matters.

C_{29} and $C_{30}\alpha\beta$-hopane occur in appreciable amount in all the Nkporo Formation and Enugu Shale samples (Fig. 4.11), indicating significant contribution of prokaryotic organisms (i.e. bacteria, cyanobacteria and blue algae) to the source organic matter.

The regular steranes /17α (H)-hopanes ratio reflects input of eukaryotic (mainly algae and higher plants) versus prokaryotic (bacteria) organisms to the source rock (Noriyuki et al,1996). The sterane/hopane ratio is relatively high in marine organic matter, with values generally approaching unity or even higher. In contrast, low steranes and sterane/hopane ratios are more indicative of terrigenous and/or microbially reworked organic matter (Noriyuki et al, 1996).

The sterane/hopane ratio values range from 0.07-0.27 for the Nkporo Formation and 0.05- 0.32 for the Enugu Shale (Table 4.11). This indicates that the studied source rock can be considered generated from terrigenous organic matter source.

The ratio values (<0.6) according to (Tissot and Welte, 1984; Peters and Moldowan, 1993; Sachsenhofer *et al.*, 1995; Norgate *et al.*, 1999) indicative of the incorporation of high level of bacterial inputs commonly associated with terrigenous organic matter in shales (non-marine organic matter).

The appreciable quantity of homohopanes (C_{31}-C_{35}) in all the samples, suggest that bacteriohopanetetrol and other polyfunctional C_{35} hopanoids; bacteriohopanepolyols, aminopolyols etc. (Wang *et al.*, 1996), common in prokaryotic micro-organisms (Ourrisson *et al.*, 1979; Rohmer, 1987) were significant contributors to the biomass.

The C_{35}/C_{30} hopane ratio values range from 0.07 to 0.21 for the Nkporo Formation and 0.1 to 0.18 for Enugu Shale, which reflects organic matter deposited in lacustrine environments (Peters *et al.*, 2005). The homohopane ratio (C35αβS/C34αβS) ranges from 0.42 to 0.79 for the Nkporo Formation and 0.38 to 0.61 for the Enugu Shale. The homohopane index (C_{35}/C_{31} - C_{35}) range from 0.04 to 0.07 for the Nkporo Formation and 0.05 to 0.06 for Enugu Shale and 0.15 to 0.92 (Table 4.11). The low homohopane index of the samples indicates oxic condition during organic matter deposition (Peters and Moldowan, 1991; Hanson *et al.*, 2001; Killops and Killops, 2005;

Peters *et al.,* 2005; Yangming *et al.,* 2005). Hopanes with αβ epimers are more prominent in all the samples while no ββ-epimer is detected. Homohopanes ranging from C_{31}-C_{35} showed notable predominance of the 22S over the 22R epimer. These observations reflect high maturity status of the samples (Miranda *et al.*, 1999; Peters *et al.*, 2005; Tuo *et al.*, 2007).

The ratio of Ts/Tm - Ts (trisnorneohopane) to Tm (trisnorhopane) of more than (0.5) increases as the portion of shale in calcareous facies increases (Hunt, 1996). Also, this ratio was proved to be useful in paleofacies predictions, though not as decisive as mature parameters. Van Grass (1990) stated that Ts/Tm ratios begin to decrease quite late during maturation, but Waples and Machihara, (1991) reported that Ts/Tm ratio does not appear to be appropriate for quantitative estimation of maturity. The Ts/Tm ratios range from 0.86 to 1.95 for the Nkporo source rock, while that of Enugu source rock range from 0.94 to 1.39 (Table 4.11). These relatively high ratios suggest that the studied source rocks were generated mainly from calcareous facies.

The Moretane/Hopane, Hopane/Hopane + Moretane and $T_s/T_s + T_m$, ratios for the Nkporo Formation range from 0.17 to 0.30; 0.77 to 0.85 and 0.51 to 0.66 respectively, while that of Enugu Shale ranges from 0.19 to 0.50, 0.67 to 0.84 and 0.48 to 0.58 respectively (Table 4.11). These values indicate samples that are within the early oil window (Peters and Moldowan, 1993; Killops and Killops, 2005; Peters *et al.,* 2005).

The abundance of C_{35} pentacyclic extended hopane seems to be associated with marine carbonates or evaporites (Riediger et al., 1990). However Peters and Moldowan (1991) prefer to correlate high C_{35}/ C_{34} ratios in marine environment with a low redox potential rather than with lithology as not all carbonate rocks have high C_{35} concentration. The concentration of C_{35} extended hopane (Fig. 4, see peak identification in Table 4.12) is more abundant in the Nkporo and Enugu Shale extracts. Such results indicate the marine input of the Nkporo and Enugu source rocks (Riediger et al., 1990). The $C_{35}/C_{30}\alpha\beta s$ hopane ratio values range from 0.42 to 0.79 for the Nkporo source rock and 0.38 to 0.61 for Enugu source rock, which reflects organic matter deposited in marine environments (Peters *et al.*, 2005) (Table 4.11).

The *m/z* 191 showing the distributions of polycyclic hydrocarbons, hopanes and homohopanes in the samples are shown in Fig. 4.47a-f and 4.48a-d of Nkporo and Enugu source rocks respectively. Peak identities are listed in Table 4.12.

Table 4.11: Source, maturity and depositional environment parameters computed from the hopane and homohopane distributions of Nkporo Formation and Enugu Shale samples

Sample No	Mortane /Hopane	Hop/Hop+ Mortane	Ts/Ts +Tm	Sterane/ Hopane	C_{35}/C_{30} Hopane	C_{29}/C_{30} Hopane	Ts/Tm	C_{35}/C_{34} αβS Hopane	Homo hopane
NKP/07	0.30	0.77	0.66	0.09	0.21	0.80	1.95	0.42	0.05
NKP/08	0.17	0.85	0.57	0.27	0.07	0.71	1.34	0.5	0.04
NKP/12	0.2	0.83	0.51	0.25	0.1	0.80	1.04	0.79	0.07
NKP/16	0.29	0.78	0.46	0.07	NIL	0.82	0.86	NIL	NIL
NKP/17	0.32	0.76	0.54	Nil	NIL	0.74	1.19	NIL	NIL
ENU/20	0.19	0.84	0.50	0.32	0.1	0.59	1.00	0.61	0.06
ENU/21	0.50	0.67	0.58	0.05	NIL	0.79	1.39	NIL	NIL
ENU/24	0.41	0.71	0.48	0.07	NIL	0.71	0.94	NIL	NIL
ENU/25	0.30	0.77	0.51	0.15	0.18	0.63	1.02	0.38	0.05

Mor/Hop = Moretane/Hopane (C30)

Hop/Hop + Mor = Hopane/Hopane + Moretane (C30)

C32HH = C32homohopane

Sterane/Hopane=C27+C28+C29steranes/[(C29+C30)αβhopane+(C31+C32+C33)αβ(R+S)homohopane]

C35/C30 = C35αβ(R+S) homohopane/ C30αβ hopane + C30βα moretane

Homohopane ratio, C35/C34 αβS = C35αβS/C34αβS homohopane

Homohopane index = C35/ C31+C32+C33+C34+C35) αβ(R+S) homohopane

NKP= Nkporo Formation

ENU= Enugu Shale

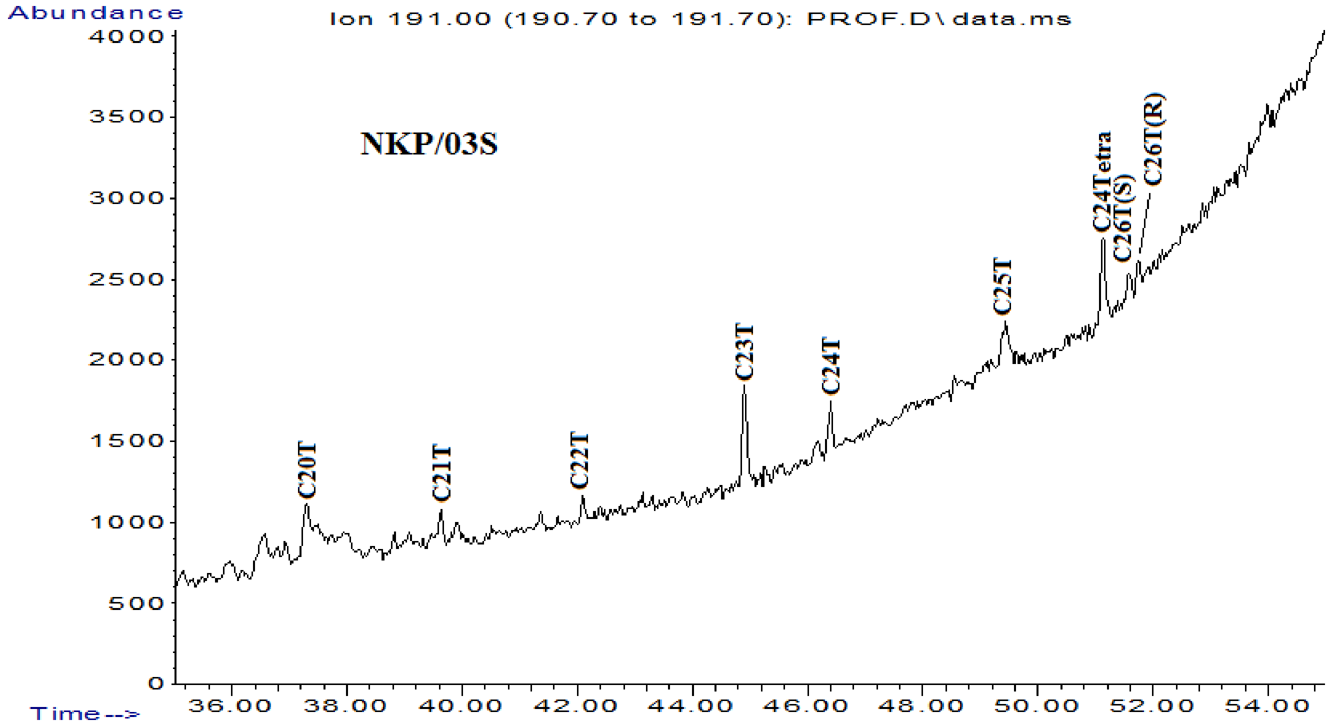

Fig. 4.47a: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/03).

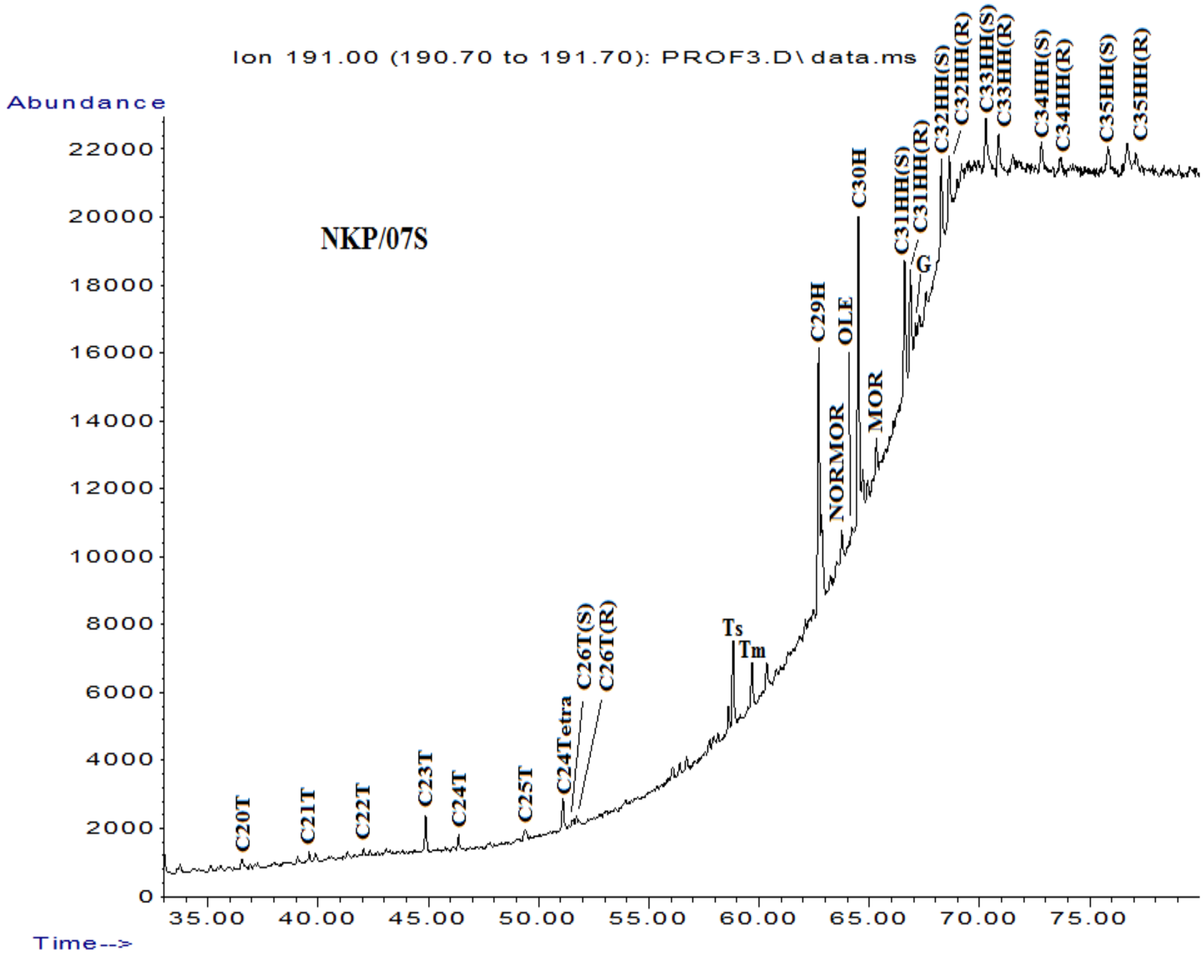

Fig. 4.47b: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/07).

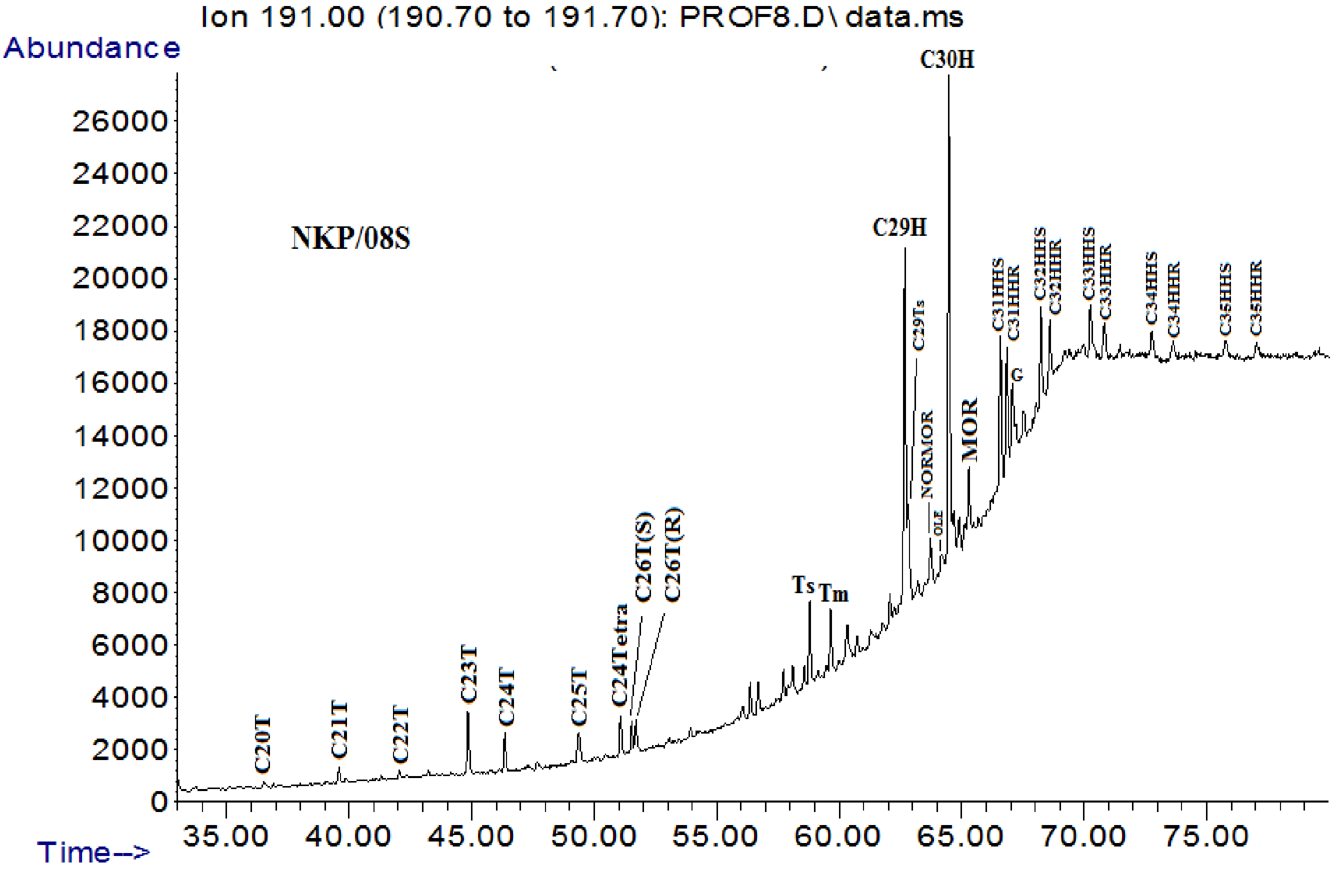

Fig. 4.47c: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/08).

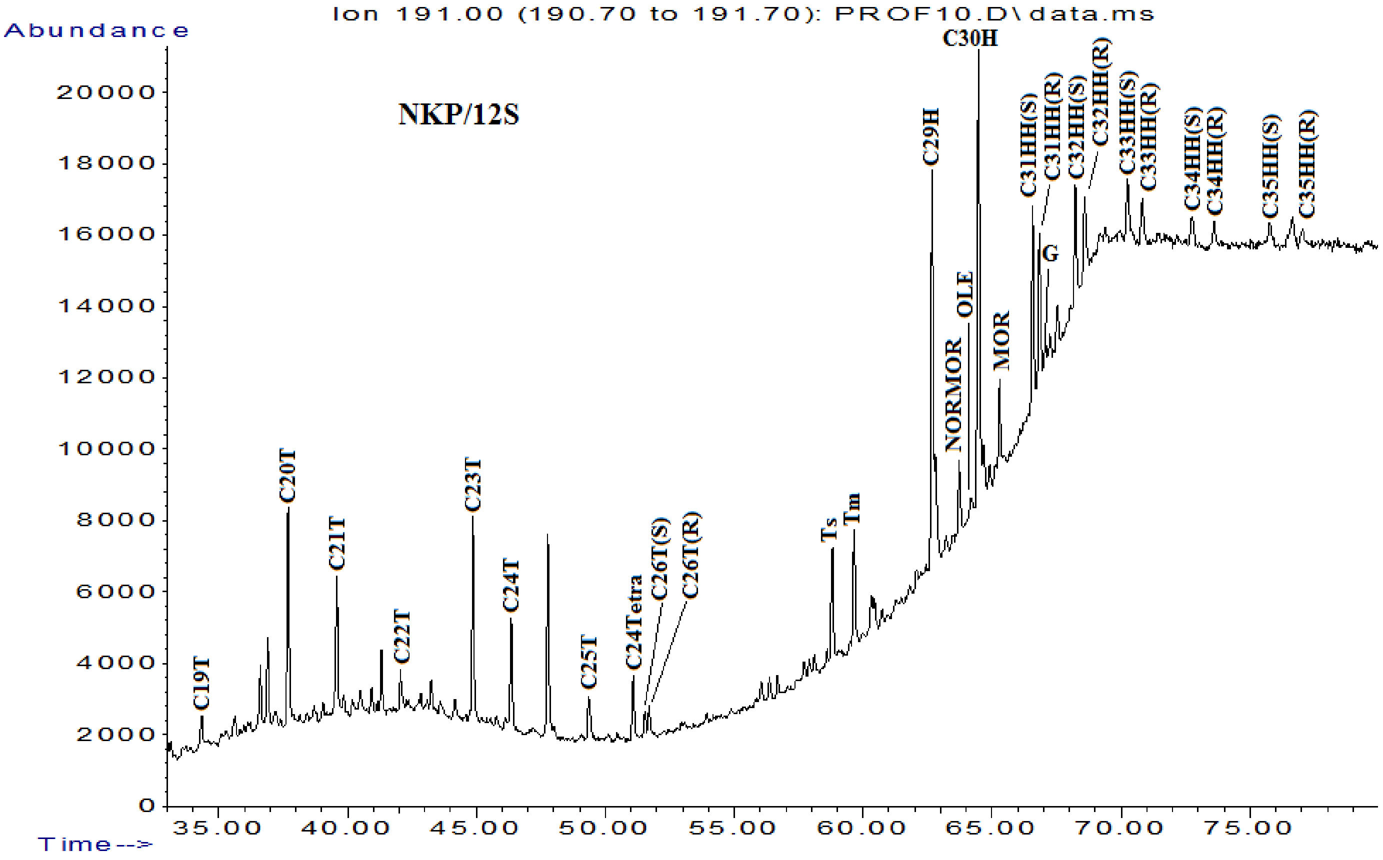

Fig. 4.47d: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/12).

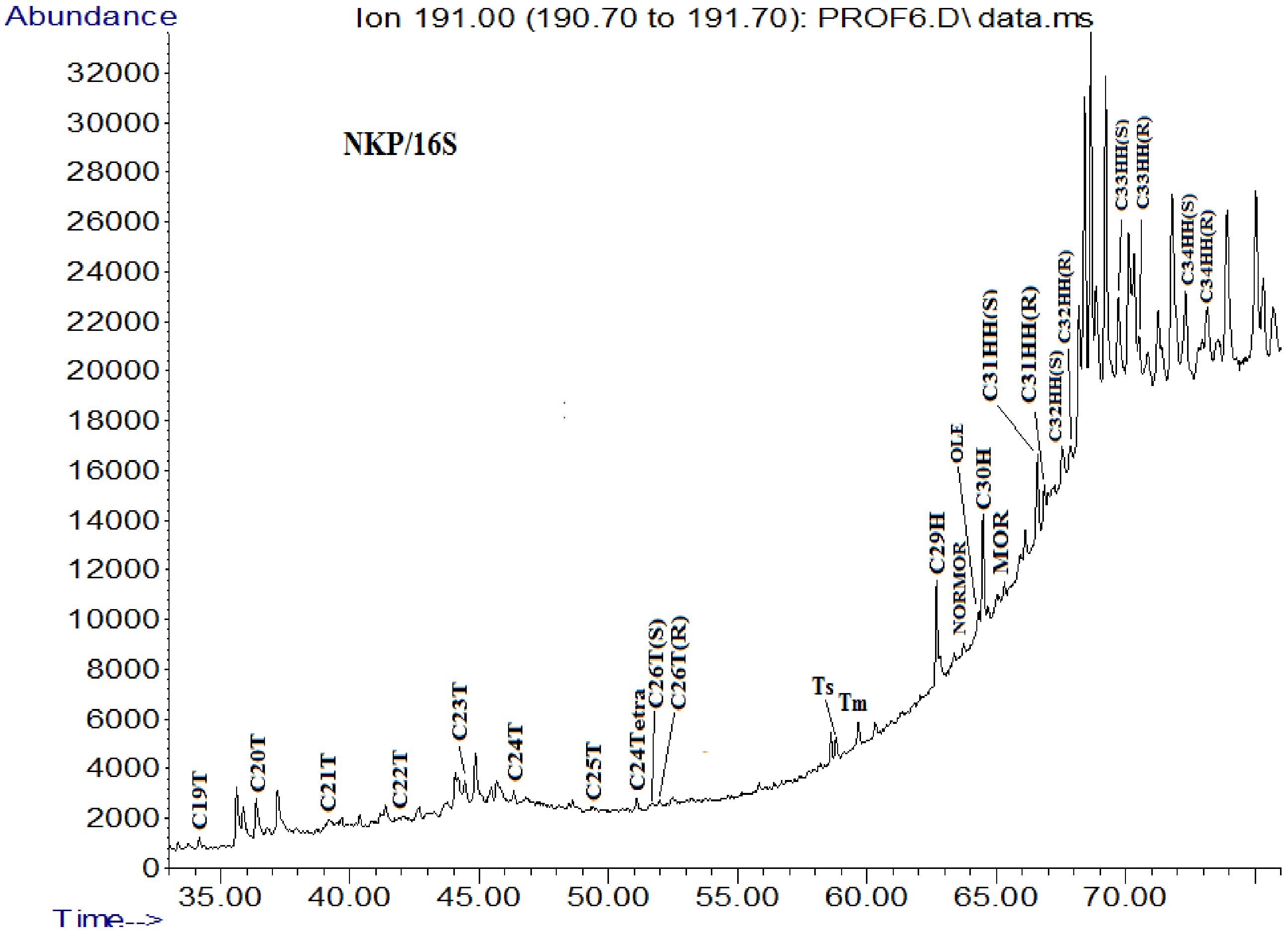

Fig. 4.47e: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/16).

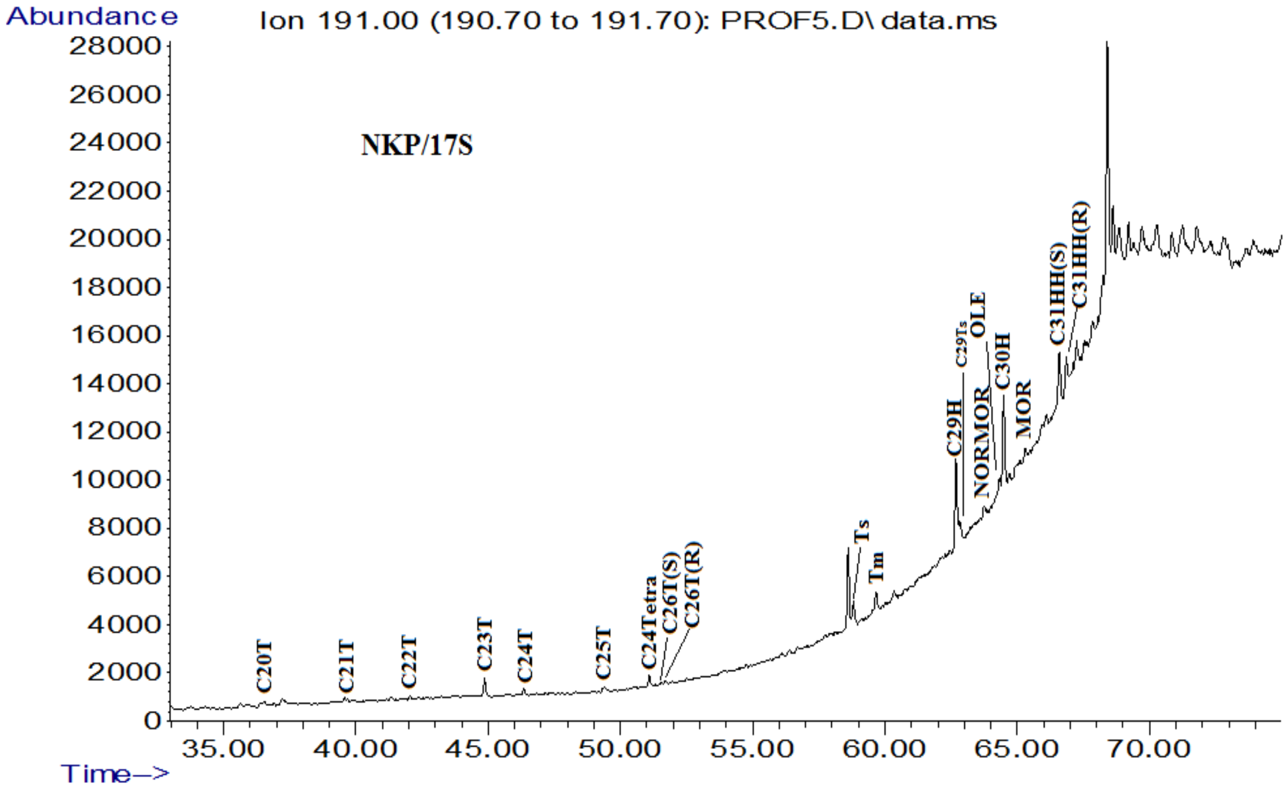

Fig. 4.47f: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Nkporo Formation (NKP/17).

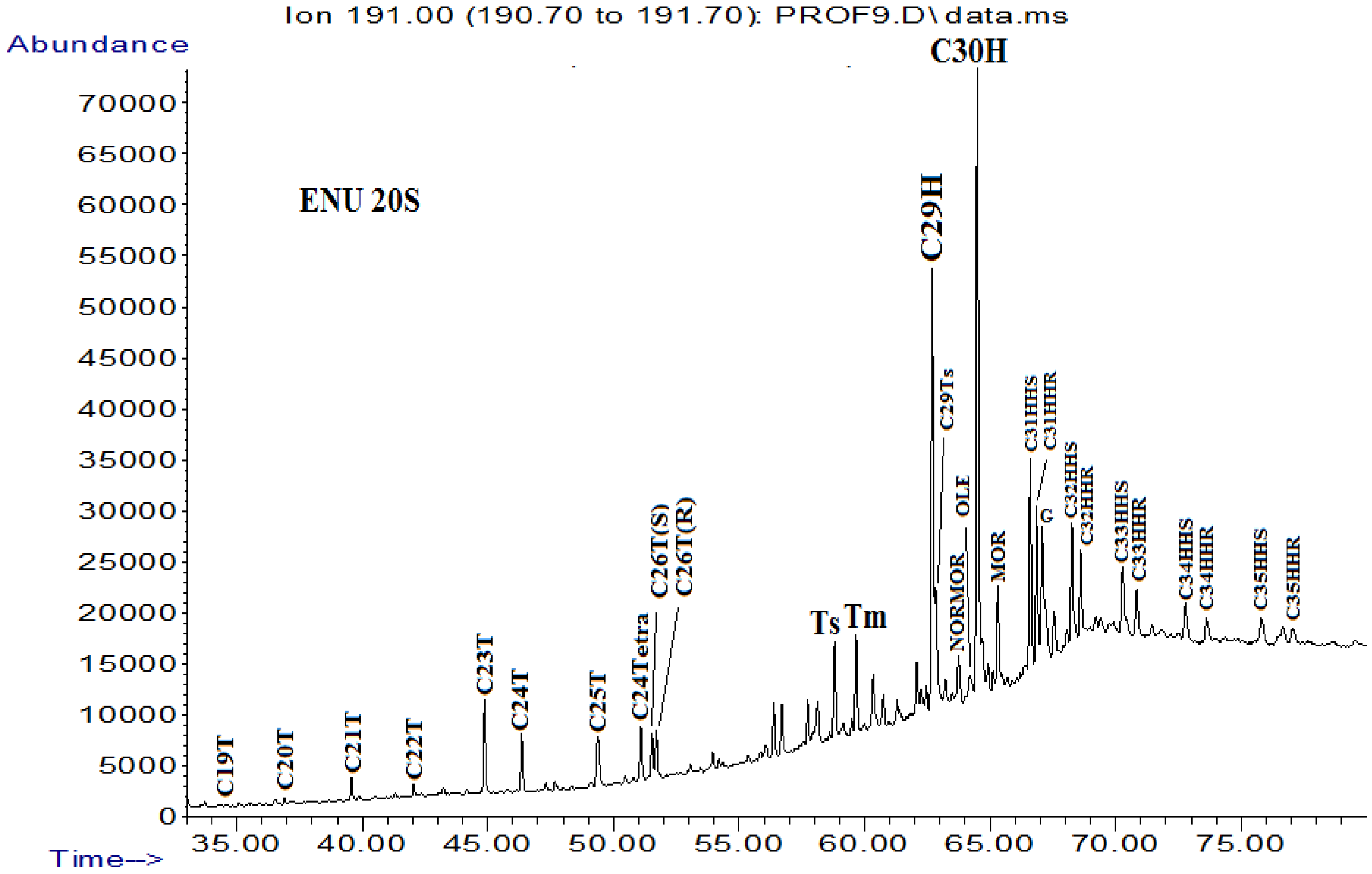

Fig. 4.48a: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/20).

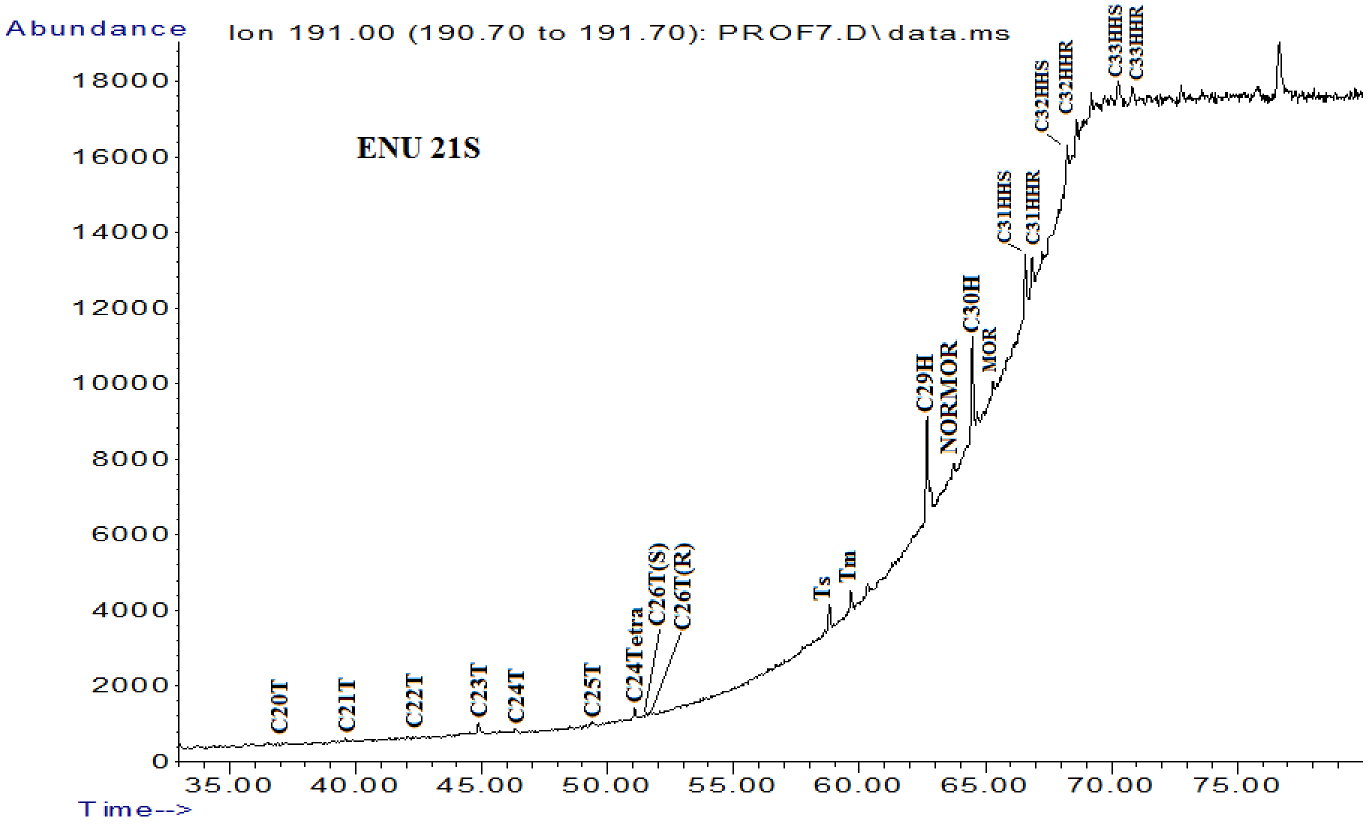

Fig. 4.48b: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/21).

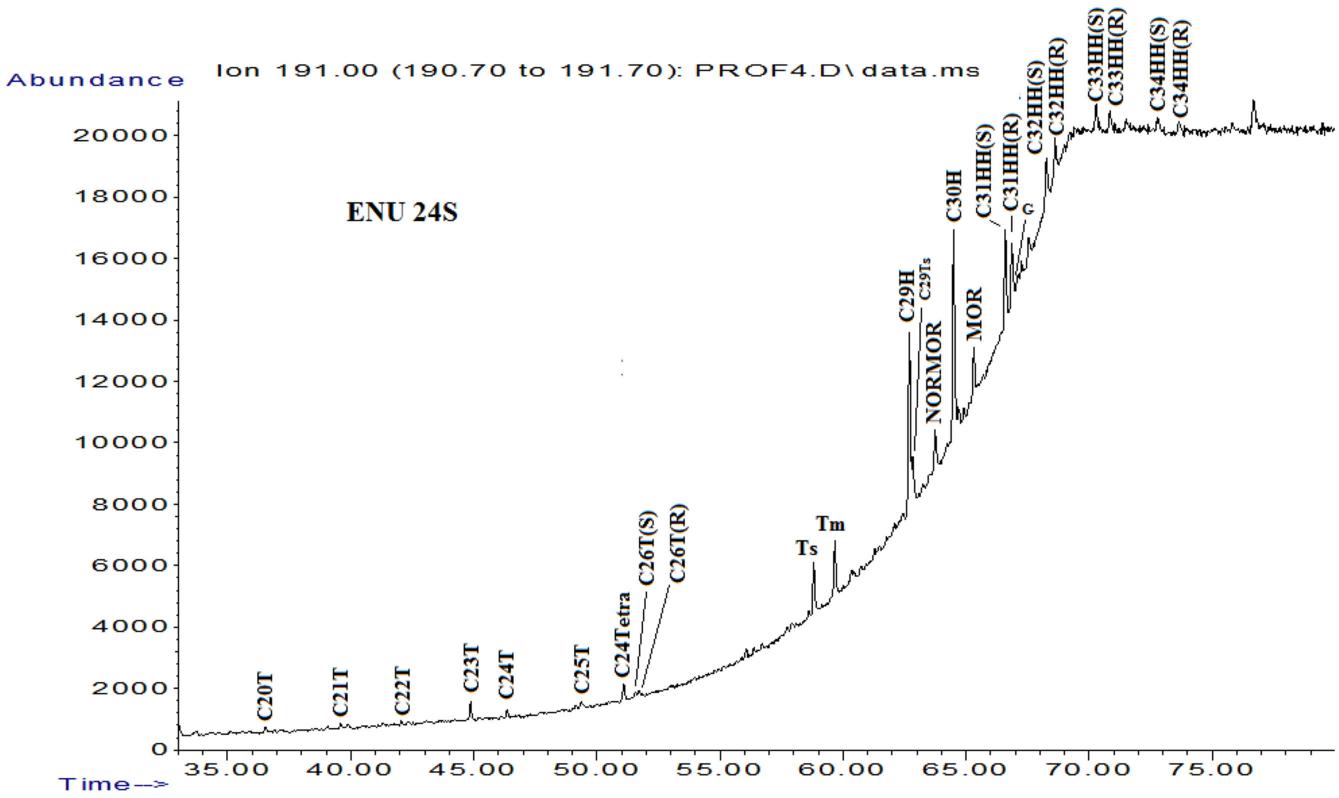

Fig. 4.48c: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/24).

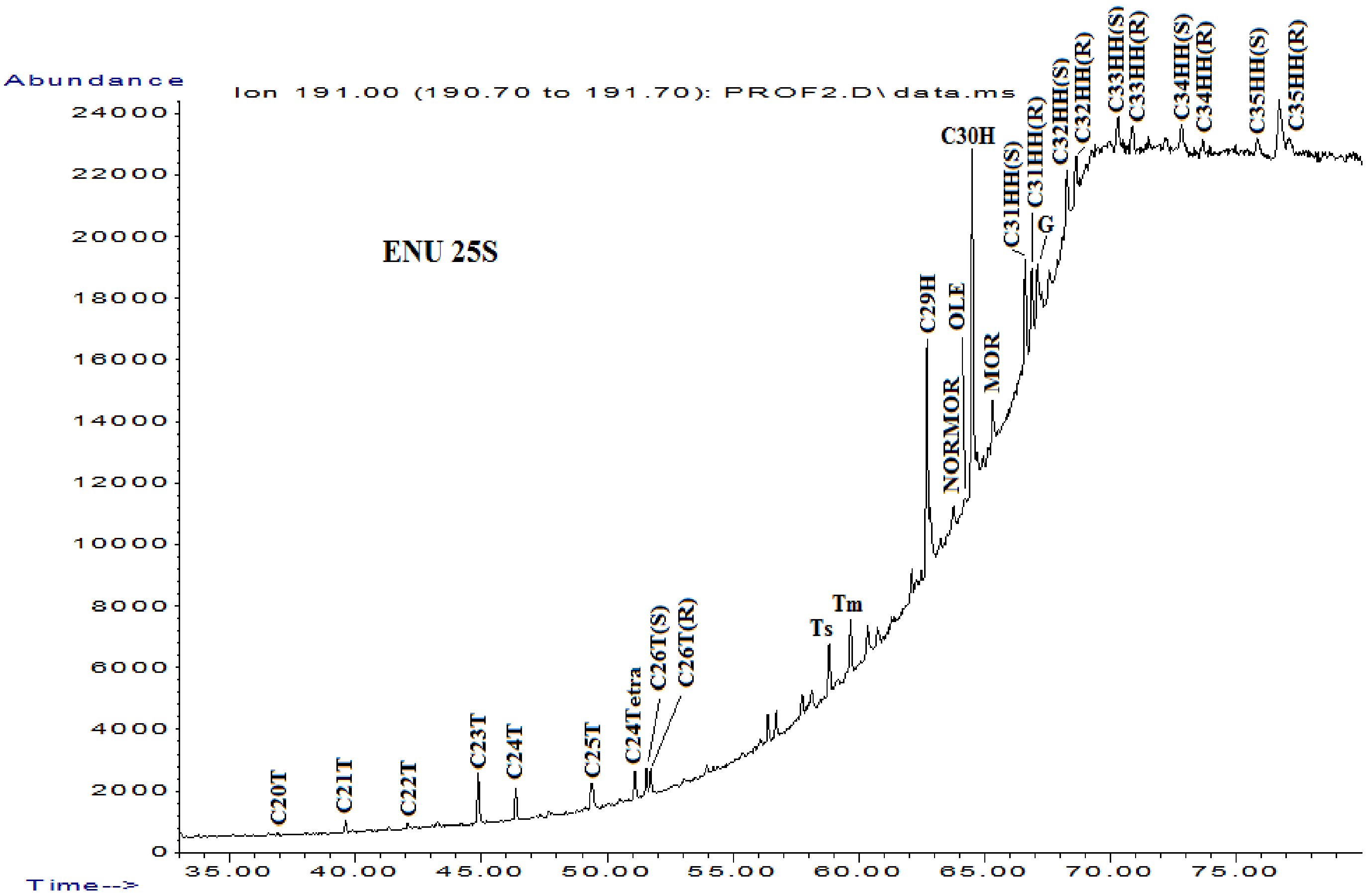

Fig. 4.48d: Mass chromatograms (m/z 191) showing the distribution of polycyclic hydrocarbon, hopanes and homohopanes in the source rock extracts of Enugu Shale (ENU/25).

Table 4.12: Peak identification of triterpenes (m/z 191) fragmentograms.

Peak	Compounds
C19tri	C19 tricyclic terpanes
C20tri	C20 tricyclic terpanes
C21tri	C21 tricyclic terpanes
C22tri	C22 tricyclic terpanes
C23tri	C23 tricyclic terpanes
C24tri	C24 tricyclic terpanes
C25tri	C25 tricyclic terpanes
C24tetra	C24 tetracyclic terpanes
C26tri	C26 tricyclic terpanes
Ts	18α(H)-22,29,30-trisnorneohopane Ts, C_{29}
Tm	17α(H)-22,29,30 Trisnorhopane Tm, C_{27}
C29H	17α(H), 21β(H)-30- norhopane C_{29}
NORMOR	Normoretane
OLE	Oleanane
C30H	17α(H), 21β(H)-hopane C_{30}
MOR	Moretane
C31HHS	22S 17α (H), 21β(H)- 30-homohopane C_{31}
C31HHR	22R 17α (H) ,21β(H)-30-homohopane C_{31}
G	Gammacerane
C32HHS	22S 17α (H) ,21β (H)-30,31-bishomohopane C_{32}
C32HHR	22R 17α(H), 21β(H)-30,31-bishomohopane C_{32}
C33HHS	22S 17α(H) 21β(H)-30,31,32-trishomohopane C_{33}
C33HHR	22R 17α(H),21β(H)-30,31,32-trishomohopane C_{33}
C34HHS	22S 17α (H) ,21β (H)-30,31-bishomohopane C_{34}
C34HHR	22R 17α(H), 21β(H)-30,31-bishomohopane C_{34}
C35HHS	22S 17α(H) 21β(H)-30,31,32-trishomohopane C_{35}
C35HHR	22R 17α(H),21β(H)-30,31,32-trishomohopane C_{35}

4.5.4 Steranes

The occurrence of C_{27} to C_{29} steranes were detected in Nkporo Formation and Enugu Shale samples. The sterane distributions for all the samples occur in the order of C_{29}>C_{28}>C_{27}. Table 4.13 show the source, maturity and depositional environment parameters computed from the sterane distributions of Nkporo Formation and Enugu Shale. The predominance of C_{27} sterane over C_{29} sterane reflects a greater input of marine relative to terrestrial organic matter. The ternary plots of sterane distribution (Fig. 4.49a and b) indicate organic matters derived from marine materials were deposited in lacustrine settings. This observation is supported by C_{27}/C_{29} ratios, which range from 0.77 to 1.13 for the Nkporo Formation samples and 0.68 to 0.80 for the Enugu Shale samples. The dominance of C_{30} steranes over dinosterol in these samples reflects typical marine source rocks.

The 20S/20S+20R and αββ/αββ+ααα C_{29} ratios range from 0.35 to 0.38 and 0.49 to 0.59 for the Nkporo Formation, while that of Enugu Shale range from 0.32 to 0.44 and 0.45 to 0.52 respectively. These values show that the samples are mature and are within the early oil generative window (Fig. 4.50a and b).

Table 4.13: Source, maturity and depositional environment parameters computed from the sterane distributions of Nkporo Formation and Enugu Shale

Sample No	%C_{27}	%C_{28}	%C_{29}	%Diasterane/ Sterane	20S/20S+20R C_{29} Steranes	Bβ/ββ+ααC29 Sterane	$C_{27}/C_{27} + C_{29}$ Sterane
NKP/ 03	nil	nil	nil	nil	nil	nil	nil
NKP/07	39.1	22.4	38.5	1.19	0.38	0.53	0.5
NKP/08	29.8	31.3	38.9	0.32	0.4	0.49	0.43
NKP/12	39	27.1	33.9	0.82	0.38	0.53	0.53
NKP/16	35.9	30.9	33.2	2.55	0.38	0.59	0.52
NKP/17	39.8	24.9	35.3	1.47	0.35	0.53	0.53
ENU/20	30.2	32.1	37.7	0.41	0.44	0.52	0.44
ENU/21	30	30.3	39.7	1.47	0.32	0.45	0.43
ENU/24	32.9	24.6	42.5	1.05	0.4	0.52	0.44
ENU/25	27.5	32.2	40.3	0.35	0.44	0.51	0.41

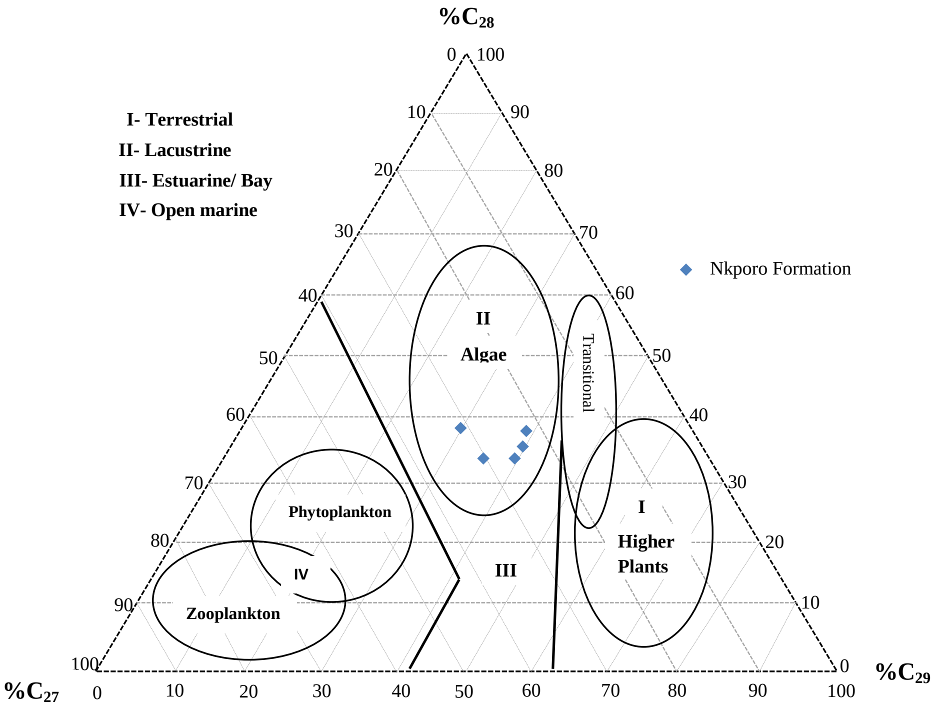

Fig. 4.49a: Ternary plot of C_{27}, C_{28} and C_{29} Steranes distribution showing the environment of deposition of Nkporo Formation samples (Peters *et al.*, 2005)

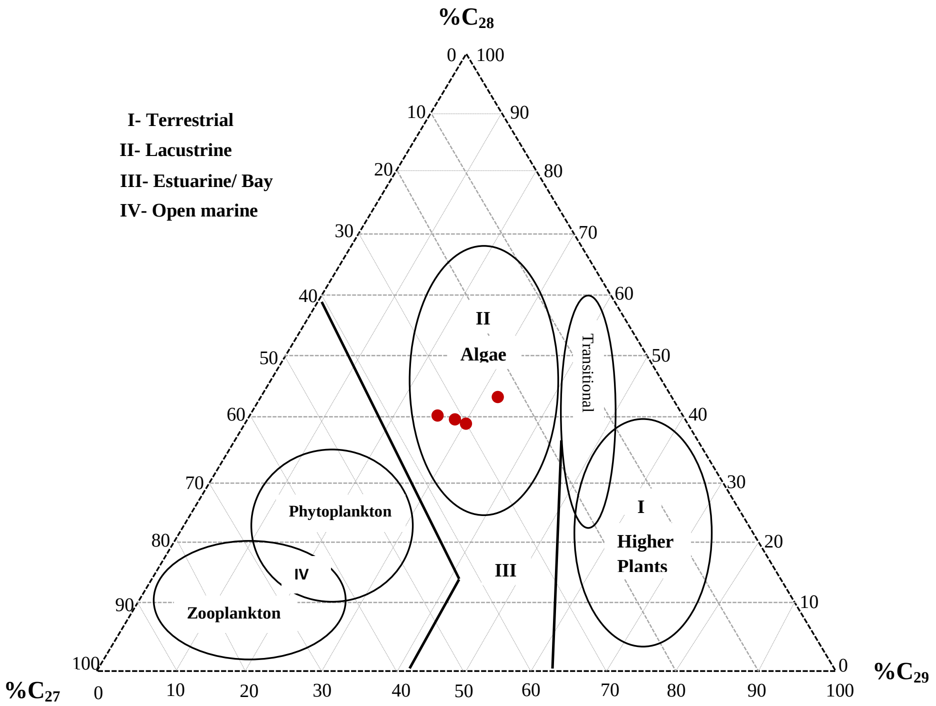

Fig. 4.49b: Ternary plot of C_{27}, C_{28} and C_{29} Steranes distribution showing the environment of deposition of Enugu Shale samples (Peters *et al.*, 2005).

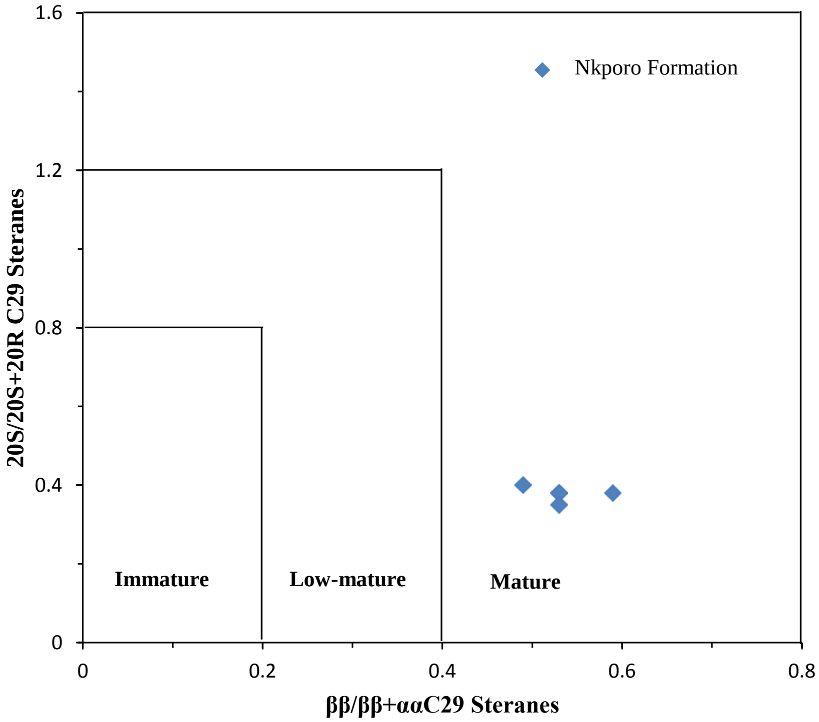

Fig. 4.50a: Plot of 20S/20S+20R versus ββ/αββ+ααα showing the thermal maturity of the Nkporo Formation samples (Killops and Killops, 2005)

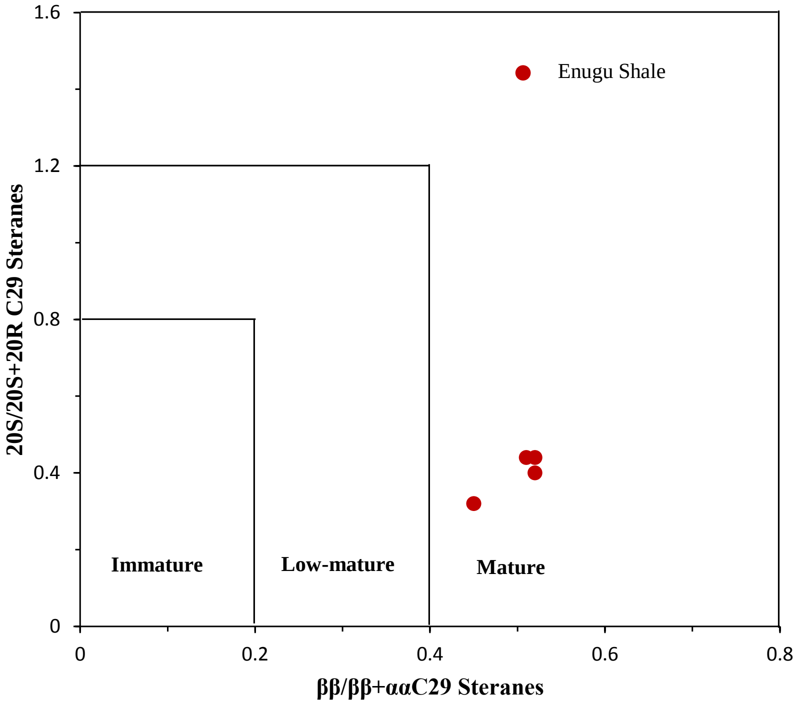

Fig. 4.50b: Plot of 20S/20S+20R versus ββ/αββ+ααα showing the thermal maturity of the Enugu Shale samples (Killops and Killops, 2005).

4.5.4.1 Ratio of sterane to Pr/Ph

Conditions of the paleodepositional environment of the source rock were evaluated using a graph of C_{27}/ (C_{27}+C_{29}) sterane versus Pr/Ph (Fig. 4.51a and b).

The C_{27}/ (C_{27}+C_{29}) sterane versus Pr/Ph ratios ranges from 0.43 to 0.53 and 0.33 to 0.78 for the Nkporo Formation which indicate that the organic matter was deposited in a pelagic and anoxic environment, while that of Enugu Shale ranges from 0.41 to 0.44 and 0.65 to 0.76 which indicate that the organic matter was deposited in a coastal and anoxic environment (Fig. 4.58a and b).

The *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in all the samples are shown in Figs. 4.52a-e and 4.53a-d. Peak identities are listed in Table 4.14.

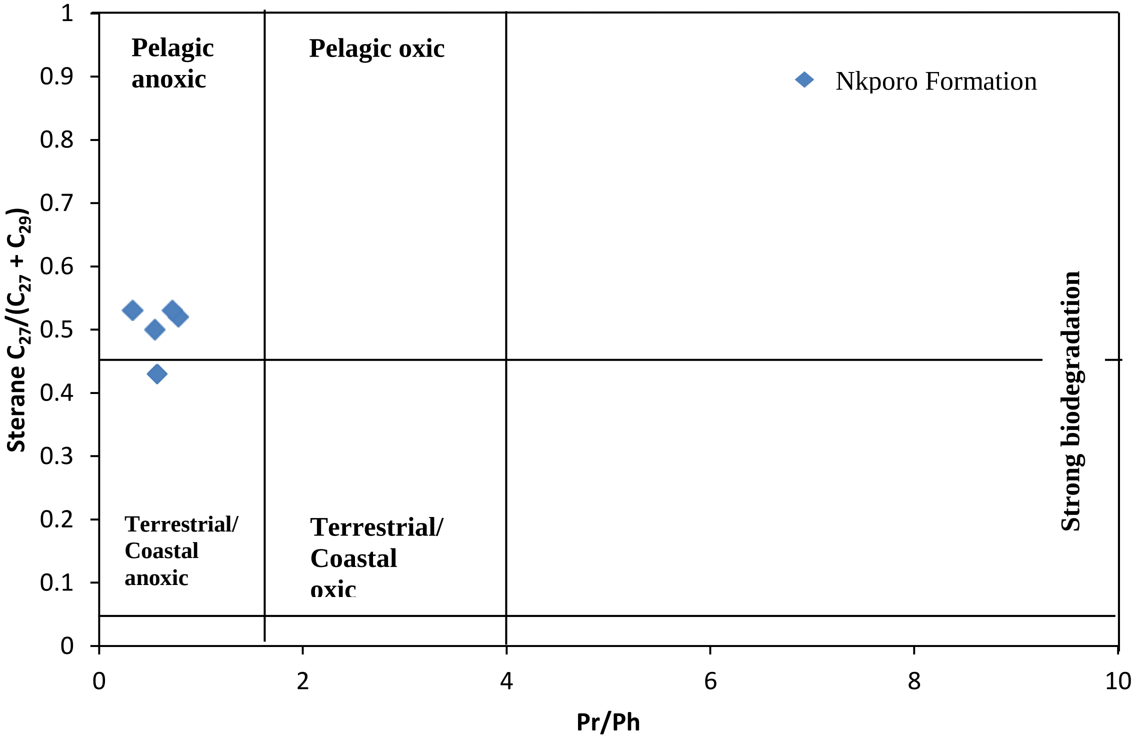

Fig. 4.51a: Plots of C_{27}/ (C_{27}+C_{29}) versus pristane/phytane ratio of the Nkporo Formation samples (Hossain *et al.*, 2009).

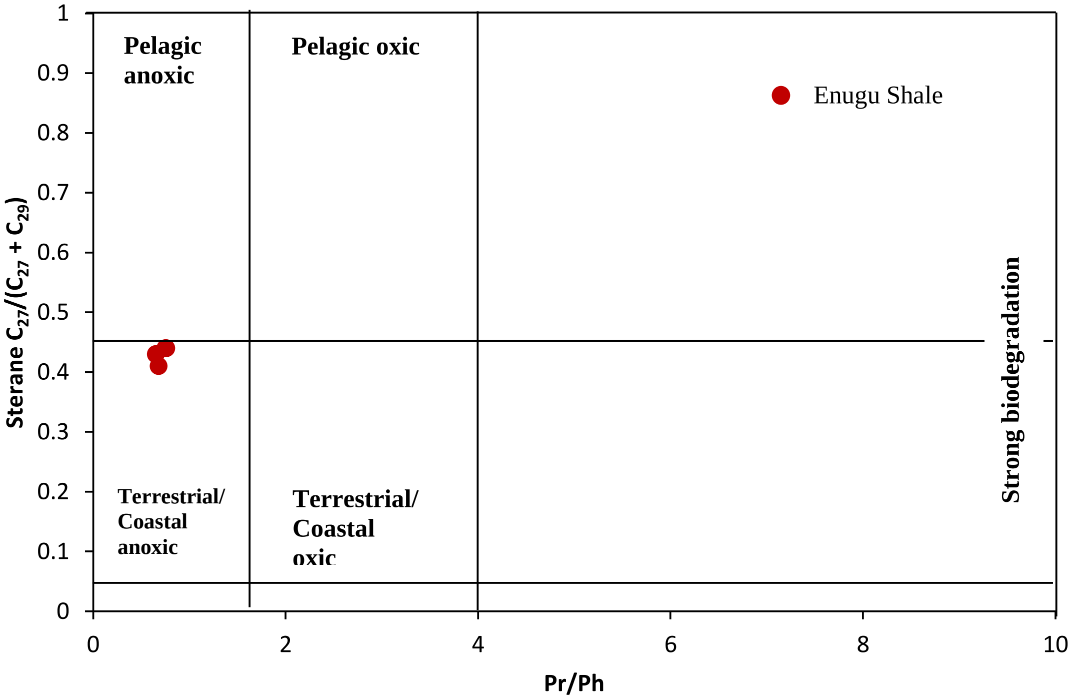

Fig. 4.51b: Plots of C_{27}/ (C_{27}+C_{29}) versus pristane/phytane ratio of the Enugu Shale samples (Hossain *et al.*, 2009).

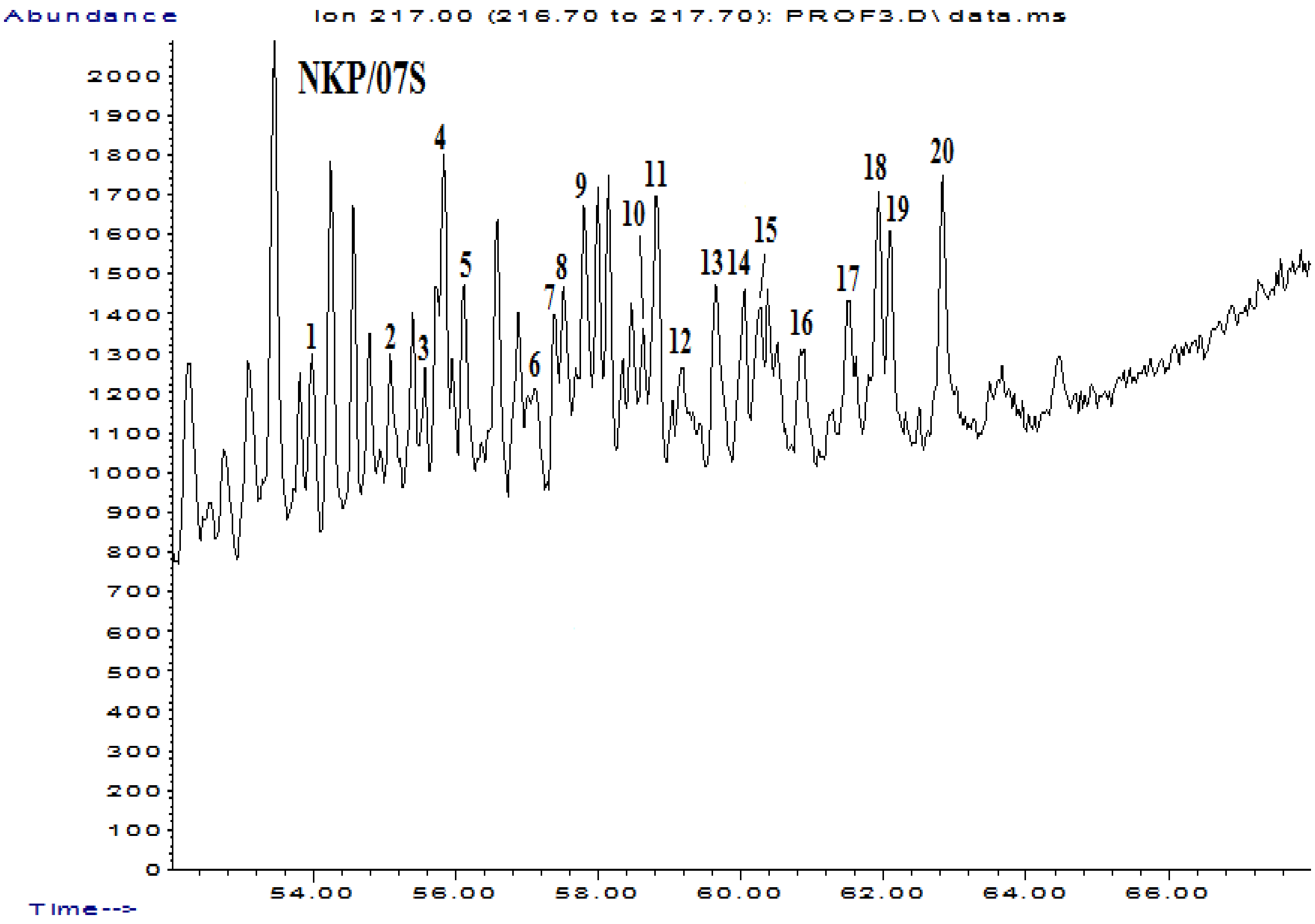

Fig. 4.52a: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/07).

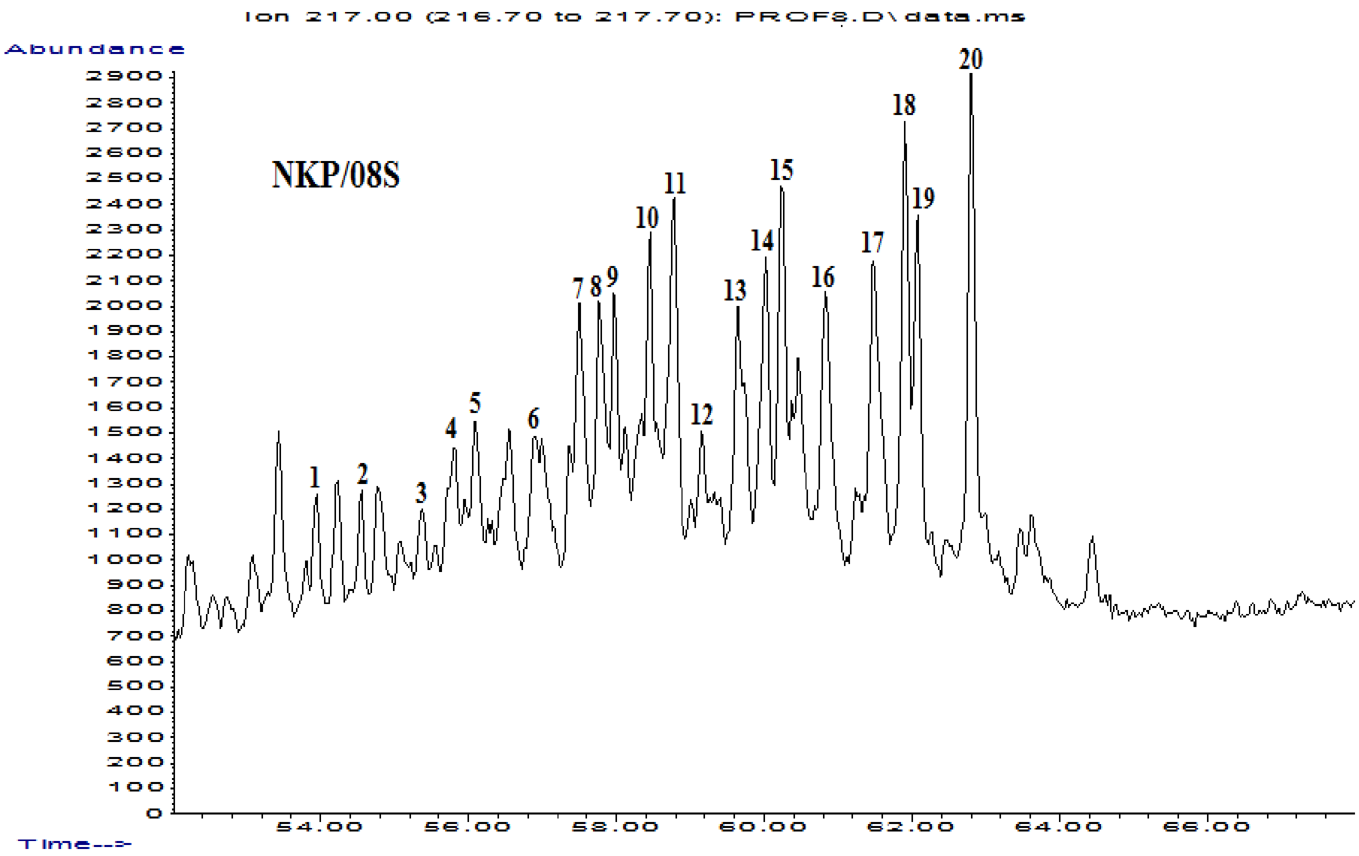

Fig. 4.52b: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/08).

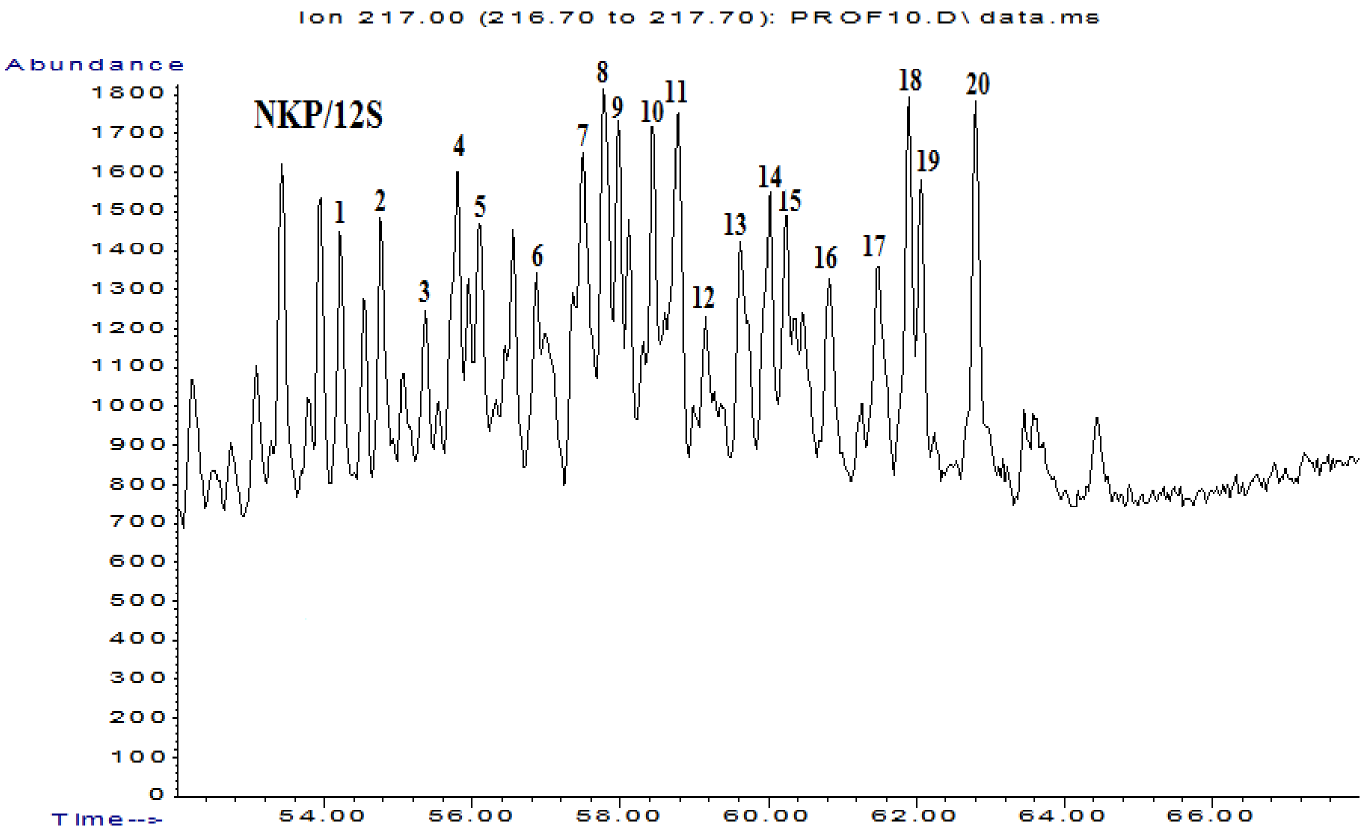

Fig. 4.52c: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/12).

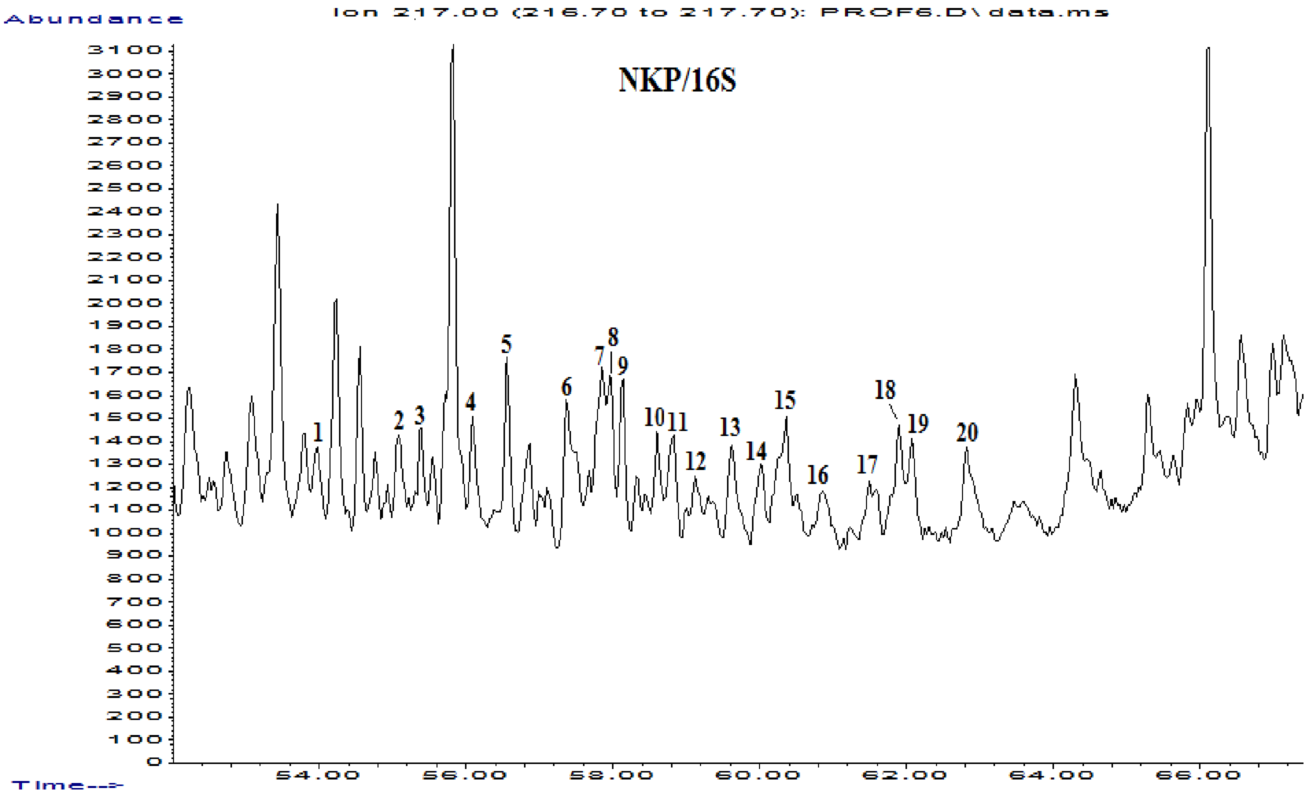

Fig. 4.52d: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/16).

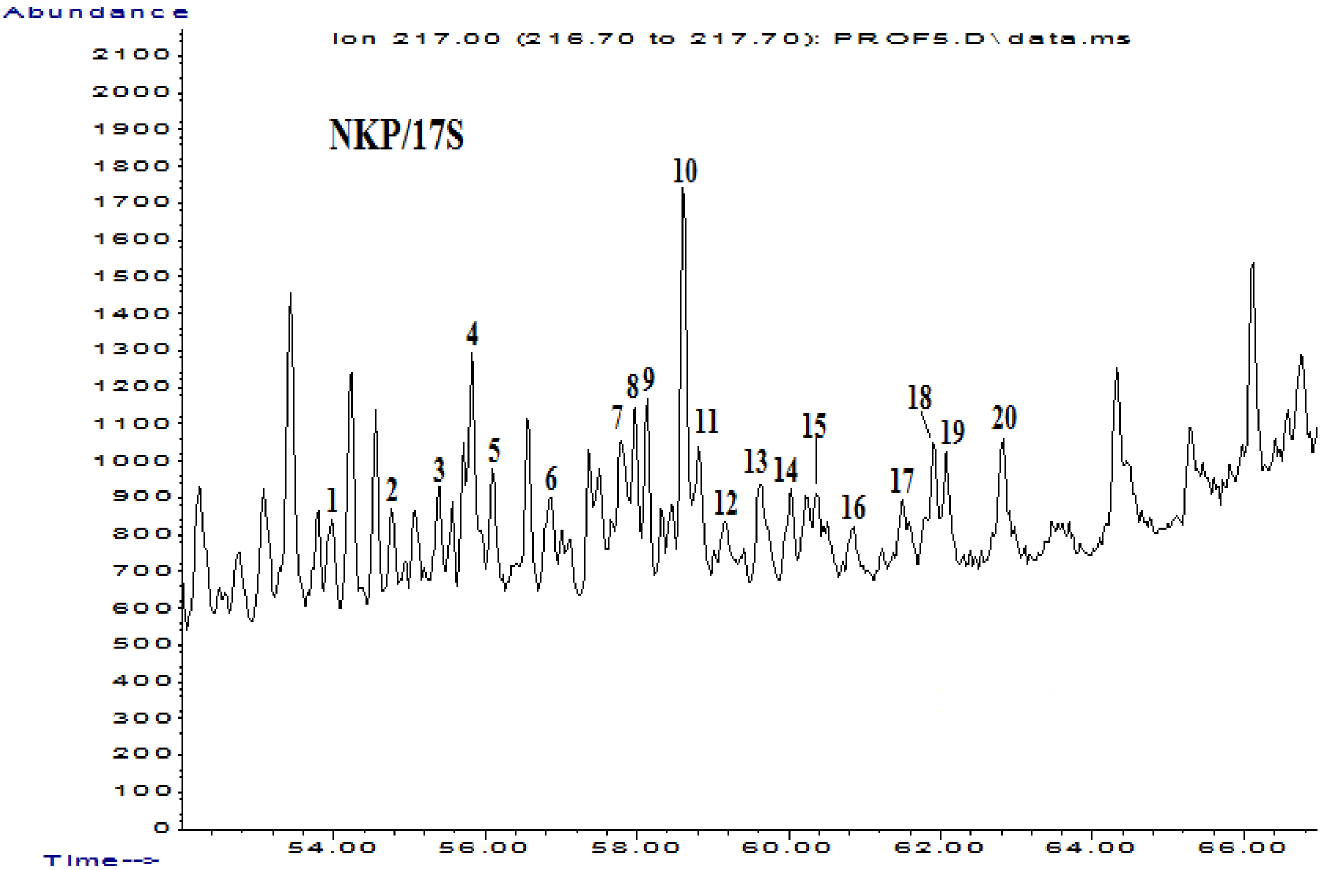

Figure 4.52e: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Nkporo Formation (NKP/17).

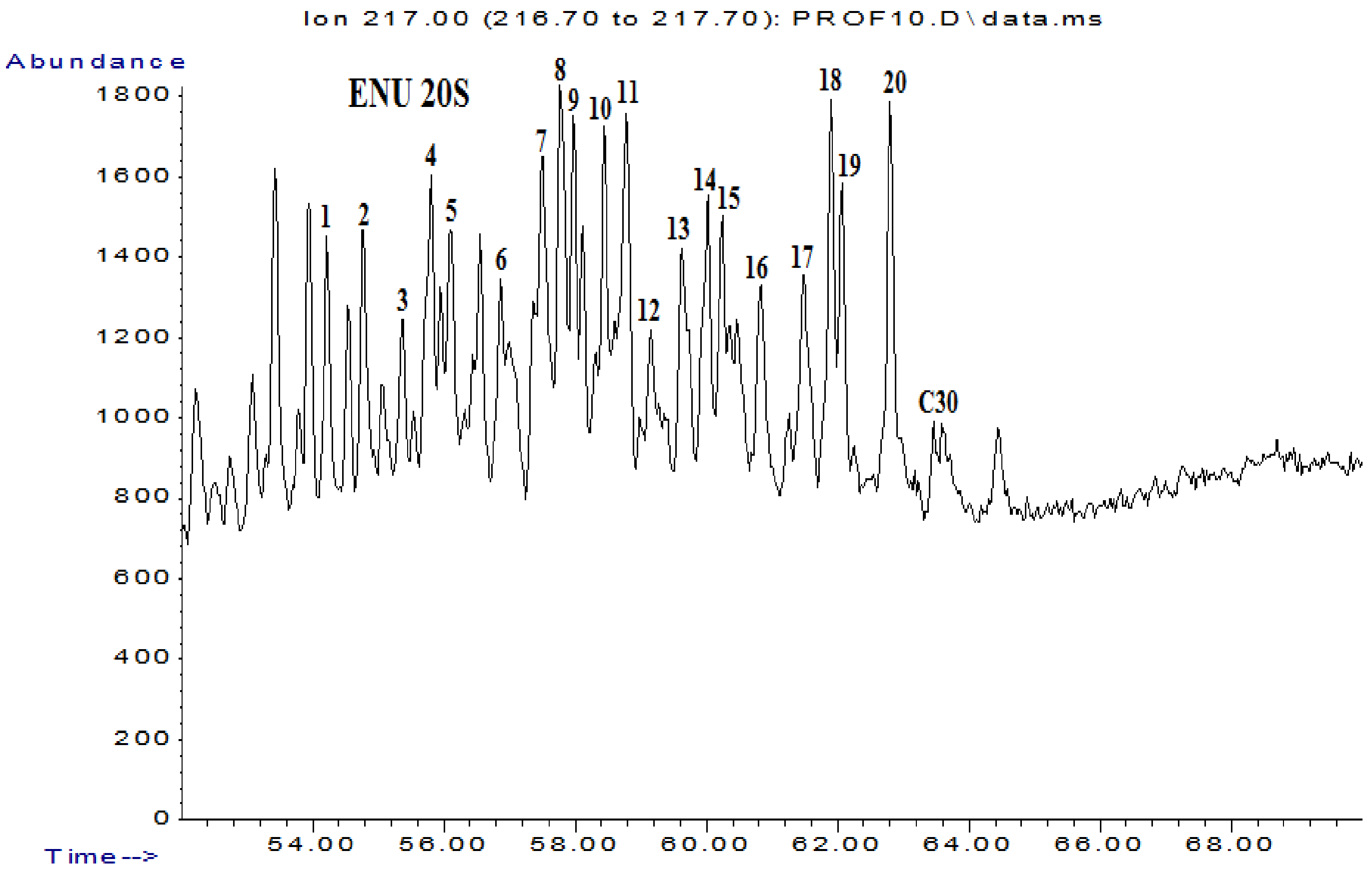

Fig. 4.53a: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/20).

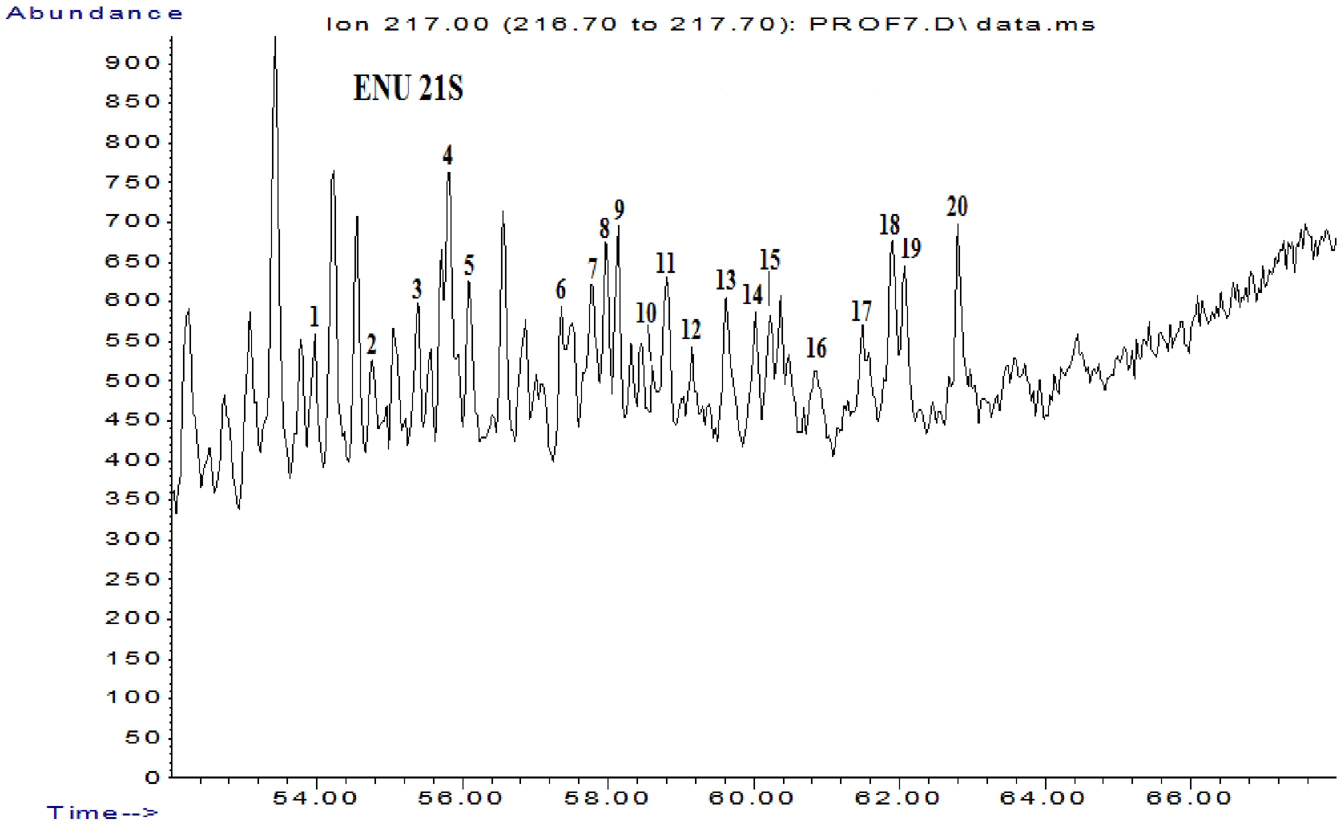

Fig. 4.53b: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/21).

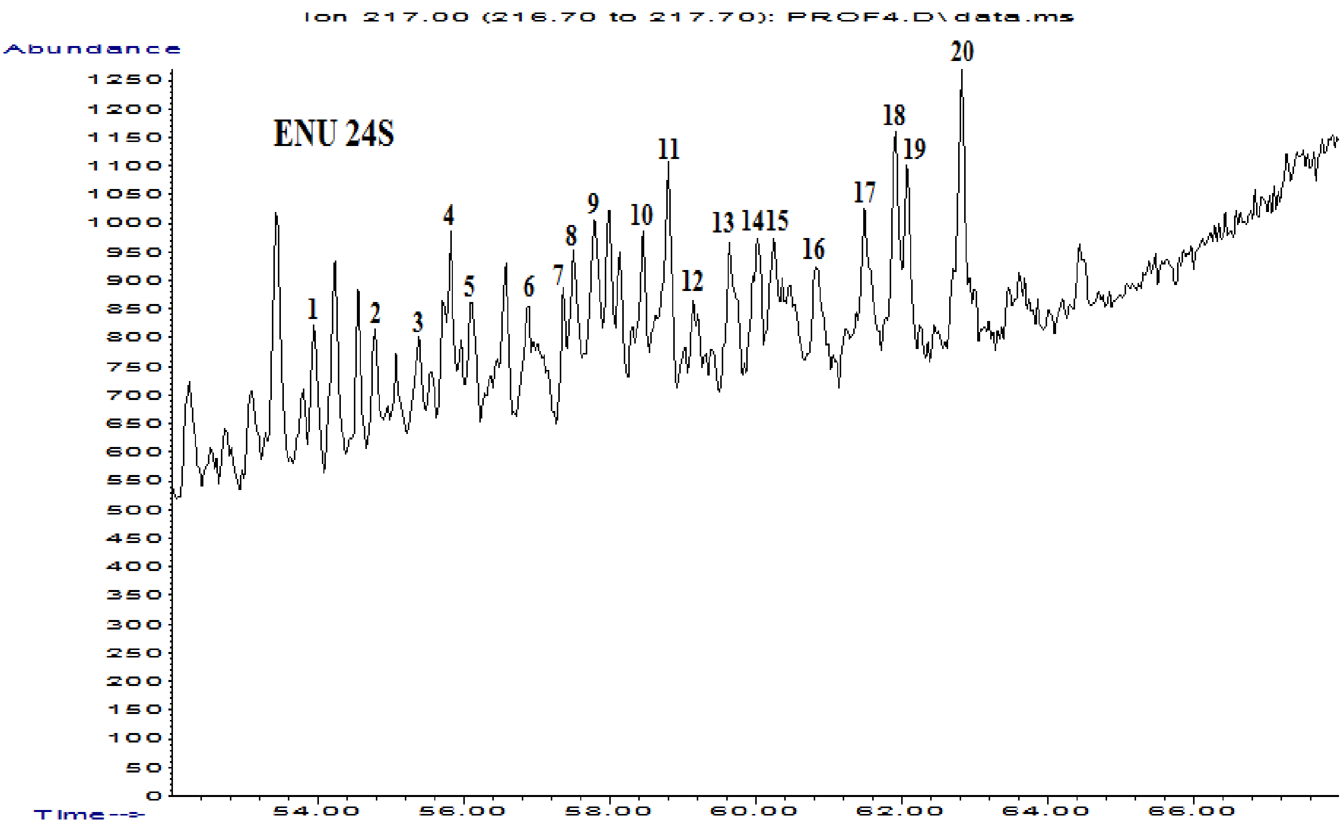

Fig. 4.53c: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/24).

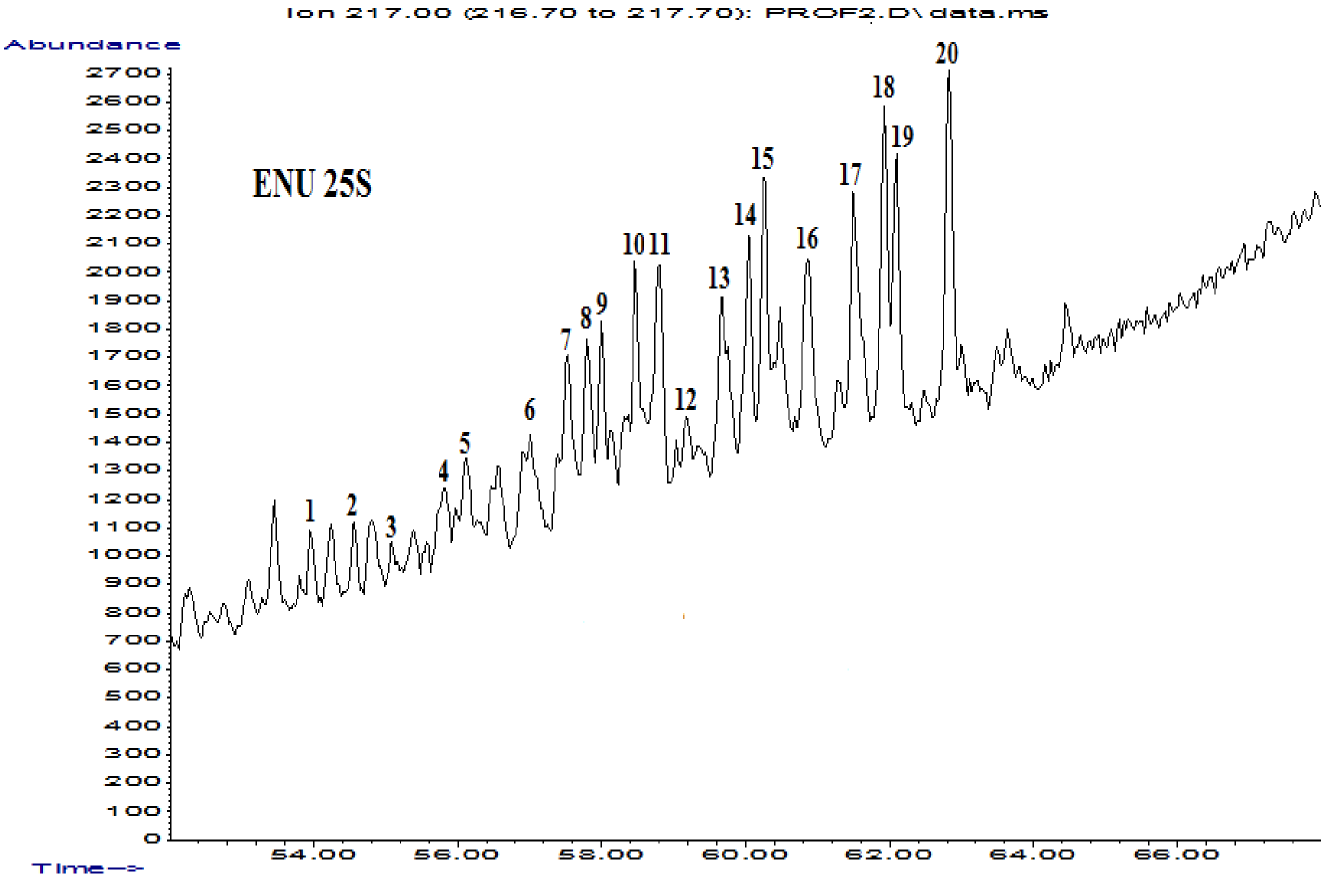

Fig. 4.53d: Mass chromatograms (m/z 217) showing the distribution of steranes in the source rock extracts of Enugu Shale (ENU/25).

Table 4.14: Peak identification of Steranes and Diasteranes (m/z 217) fragmentograms.

Peak	Compounds
1	20S 13β, 17α-diacholestane C_{27}
2	20R 13β, 17α-diacholestane C_{27}
3	20S 13α,17β-diacholestane C_{27}
4	20S 24-methyl-13β,17α-diacholestane C_{28}
5	20R 24-methyl-13β,17α-diacholestane C_{28}
6	20R 24 methyl -13β,17α-diacholestane C_{28}
7	20R 24 methyl -13α,17β-diacholestane C_{28} + 20S 14α,17α cholestane C_{27}
8	20S 24 ethyl -13β,17α-diacholestane C_{29} + 20R 14β,17β cholestane C_{27}
9	20R 24 methyl -13α,17β-diacholestane C_{28} + 20S 14β,17β cholestane C_{27}
10	20R 14α,17α-cholestane C_{27}
11	20R 24-ethyl-13β,17α-diacholestane C_{29}
12	20S 24-ethyl-13α,17β-diacholestane C_{29}
13	20S 24-methyl-14α,17α-cholestane C_{28}
14	20R 24-methyl-14β,17β-cholestane C_{28}
15	24-methyl-14α,17α-cholestane C_{28}
16	20R 24-methyl-14α,17α-cholestane C_{28}
17	20S 24-ethyl-14α,17β-cholestane C_{29}
18	20R 24-ethyl-14β,17α-cholestane C_{29}
19	20S 24-ethyl-14β,17β-cholestane C_{29}
20	20R 24-ethyl-14α,17α-cholestane C29
C30	C_{30} sterane

4.6 Palynological Analysis

Interpretation of Results

4.6.1 Age Determination

The age determination of the examined samples was based on selected key age-diagnostic palynomorph assemblages encountered. They are summarized as follow:

From the tables 4.15a-d, samples NKP/09/002, NKP/07/001, NKP/13/001, NKP/12/001, NKP/03/002, NKP/04/001, NKP/06/001, NKP/10/001, NKP/08/001, NKP/01/001, and NKP/15/001, NKP/16/002, ENU/23/001, ENU/24/001, ENU/25/001and ENU/27/001, were dated Late Campanian to Earliest Maastrichtian with the following sporomorphs assemblage: *Foveotriletes margaritae, Distaverrusporites simplex, Cingulatisporites ornatus, Echitriporites trianguliformis, Longapertites marginatus, Proteacidites segali, Monocolpites marginatus, Constructipollenites ineffectus, Buttinia andreevi, and Retidiporites magdalenensis,* (Lawal and Moullade, 1968; Umeji, 2007, 2011; and Chiaghanam *et al*, 2012). The age was further confirmed by the presence of the typical West African Campano-Maastrichtian Dinocysts assemblage such as, *Dinogymnium* sp., *Andalusiella polymorpha, Andalusiella manthei*, *Senegalinium* sp., *Ceratiopsis diebeli,* and *Paleocystodinium austrialinium,* (Lentin and Williams, 1978; May, 1980) (Fig. 4.77).

1. Meanwhile, samples NKP/LST/05/001, and NKP/14/001 lack adequate marker palynomorph assemblages required for proper age assessment. However, based on some few important palynomorphs species recovered, sample NKP/14/001 has tentatively been assigned Late Campanian age whereas NKP/LST/05/001 were probably assigned Late Campaniam – Earliest Maastrichtian, (Table 4.15a and b).

2. However, samples NKP/16/004, NKP/16/008, NKP/17/001, NKP/17/003, ENU/20/001, ENU/21/003, and ENU/22/001, were assigned to Early Maastrichtian based on *Longapertites*

marginatus (overwhelming abundance), *Longapertites microfoveolatus, Longapertites vaneedenburgi, Spinizonocolpites baculatus*, *Foveotriletes margaritae, Distaverrusporites simplex, Cingulatisporites ornatus, Matonisporites equiexinus, Azolla marsulae*, *Mauritidiites crassibaculatus, Constructipollenites ineffectus, Echitriporites trianguliformis, Foveotriletes margaritae*, and *Leiotriletes minor* (Lawal and Moullade, 1968; Umeji, 2007, 2011; Ogalla, 2009; and Chiaghanam *et al*, 2012) (Tables 4.15c and d).

Fig. 4.54 show the micrograph pictures of some key palynomorphs species recovered from the analyzed samples. Table 4.27 show the micrograph names of some palynomorph species recovered in the examined samples.

Table 4.15a: The occurrence and distribution of palynomorphs species in the examined samples

Sample No. / Palynomorphs species	NKP/01/003	NKP/03/002	NKP/04/001	NKP/LST/05	NKP/06/001	NKP/07/001	NKP/08/001
TERRESTRIAL SPECIES							
Spores							
Foveotriletes margaritae	-	1	-	-	2	1	-
Laevigatosporites ovatus	9	13	9	3	8	6	13
Cyathidites minor	4	-	2	-	1	-	-
Cyathidites australis	-	8	4	2	2	3	-
Leiotriletes adriennis	2	3	-	-	-	5	-
Verrucatosporites usmensis	-	4	1	-	3	-	-
Cingulatisporites ornatus	2	4	2	-	5	3	4
Distaverrusporites simplex	1	1	3	-	-	1	-
Leiotriletes minor	3	-	2	2	3	-	-
Schizosporis parvus	-	-	-	-	-	-	-
Pollen							
Buttinia andreevi	3	-	-	-	-	-	2
Proxapertites operculatus	-	2	1	-	3	1	2
Echitriporites trianguliformis	4	3	2	-	5	3	2
Retidiporites magdalenensis	2	-	-	-	1	1	4
Spinizonocolpites baculatus	-	-	1	-	-	3	2
Grimsdalea polygonalis	-	-	-	-	-	-	-
Longapertites marginatus	8	6	4	3	7	5	12
Constructipollenites ineffectus	2	-	1	-	-	1	6
Monoporites annulatus	2	7	3	2	5	3	8
Spinizonocolpites echinatus	3	5	3	-	1	1	4
Monocolpites marginatus	-	2	-	-	-	-	-
Mauritidiites crassibaculatus	2	1	-	-	-	2	-
Proxapertites cursus	-	-	1	-	2	-	-
Proteacidites segali	-	1	2	-	-	-	-
Psiltricolporites crassus	-	3	4	-	2	-	4
Psilatricolporites operculatus	2	1	-	-	3	-	-
Echitriporites trianguliformis	1	-	2	-	4	2	-
Pachydermites diederixi	-	-	-	-	-	-	2
Echiperiporites icacinoides	2	4	2	2	-	-	-
Zlivisporis blanensis	-	-	-	-	-	-	-
MARINE SPECIES							
Andalusiella polymorpha	2	-	1	-	-	5	2
Ceratiopsis diebeli	-	-	2	1	1	7	-
Senegaliniun sp.	4	-	-	-	2	14	-
Fibrocysta sp.	-	-	-	-	-	6	-
Phelodinium sp.	2	1	-	-	4	11	-
Cordosphaeridium sp.	-	-	2	-	2	4	-
Paleocystodinium austrialinium	6	-	-	2	-	6	4
Dinogymnium acuminatum	2	-	-	-	-	4	6
Spiniferites sp.	-	5	3	-	1	-	-
Oligosphaeridium complex	-	-	1	-	-	4	2
Andalusiella manthei	2	-	-	2	-	1	-
Senoniasphaera inornata	-	-	-	-	-	-	-
Glaphyrocysta ordinate	-	-	-	-	-	-	-

Table 4.15b: The occurrence and distribution of palynomorphs species in the examined samples

Sample No. **Palynomorphs species**	NKP/09/002	NKP/10/001	NKP/12/001	NKP/13/001	NKP/14/001	NKP/15/001
TERRESTRIAL SPECIES						
Spores						
Foveotriletes margaritae	2	-	-	-	-	1
Laevigatosporites ovatus	4	6	11	16	8	7
Cyathidites minor	2	6	4	4	-	-
Cyathidites austrialis	-	-	-	-	-	2
Leiotriletes adriennis	8	2	2	-	-	-
Verrucatosporites usmensis	-	-	-	-	-	-
Cingulatisporites ornatus	2	12	-	-	2	-
Distaverrusporites simplex	-	6	-	-	-	-
Leiotriletes minor	-	-	4	-	-	4
Schizosporis parvus	-	-	3	-	-	-
Pollen						
Buttinia andreevi	-	-	-	2	-	-
Proxapertites operculatus	2	-	2	2	-	-
Echitriporites trianguliformis	2	-	4	-	-	1
Retidiporites magdalenensis	4	-	-	-	-	-
Spinizonocolpites baculatus	6	-	2	2	-	-
Grimsdalea polygonalis	2	-	-	-	-	-
Longapertites marginatus	6	3	8	6	4	4
Constructipollenites ineffectus	2	-	-	1	-	-
Monoporites annulatus	2	-	2	-	-	3
Spinizonocolpites echinatus	2	2	-	-	-	-
Monocolpites marginatus	2	2	-	-	2	2
Mauritidiites crassibaculatus	4	-	2	-	-	-
Proxapertites cursus	-	-	2	-	-	2
Proteacidites segali	-	-	2	-	2	-
Psiltricolporites crassus	-	2	-	-	2	1
Psilatricolporites operculatus	-	2	-	-	-	-
Echitricolporites spinosus	-	2	-	-	-	1
Pachydermites diederixi	-	-	-	-	-	-
Echiperiporites icacinoides	-	-	-	2	-	4
Zlivisporis blanensis	-	-	1	-	-	1
MARINE SPECIES						
Andalusiella polymorpha	8	4	-	4	-	-
Ceratiopsis diebeli	14	-	-	-	-	-
Senegaliniun sp.	22	-	-	6	-	2
Fibrocysta sp.	12	-	9	-	-	-
Phelodinium sp.	22	-	2	4	-	4
Cordosphaeridium sp.	6	-	17	-	-	2
Paleocystodinium austrialinium	4	-	-	2	-	-
Dinogymnium acuminatum	6	-	-	-	-	-
Spiniferites sp.	2	2	-	-	-	2
Oligosphaeridium complex	6	2	-	-	-	-
Andalusiella manthei	2	-	-	-	-	2
Senoniasphaera inornata	-	-	2	-	-	-
Glaphyrocysta ordinate	-	-	4	-	2	3
Aleorigera senoniensis	-	-	-		2	-
Achomosphaera ramulifera	-	2	-		-	1
Cyclonepheliun deckonincki	-	2	-		-	-
Kallosphaeridium brevibarbatum	-	1	-		-	-

Table 4.15c: The occurrence and distribution of palynomorphs species in the examined samples

Sample No. / Palynomorphs species	NKP/16/002	NKP/16/004	NKP/16/008	NKP/17/001	NKP/17/003
TERRESTRIAL SPECIES					
Spores					
Foveotriletes margaritae	-	-	-	-	2
Laevigatosporites ovatus	16	11	26	10	16
Cyathidites minor	2	-	-	2	2
Cyathidites austrialis	-	3	-	2	-
Leiotriletes adriennis	-	1	2	-	-
Verrucatosporites usmensis	-	-	-	-	2
Cingulatisporites ornatus	1	1	2	2	-
Distaverrusporites simplex	2	-	-	-	-
Leiotriletes minor	-	3	-	1	-
Azolla marsulae	-	-	2	-	-
Matonisporites equiexinus	-	-	-	-	2
Pollen					
Buttinia andreevi	2	-	-	2	-
Proxapertites operculatus	-	-	2	-	-
Echitriporites trianguliformis	2	1	-	2	4
Retidiporites magdalenensis	2	1	4	-	2
Spinizonocolpites baculatus	-	-	-	-	2
Longapertites microfoveolatus	-	-	-	-	-
Longapertites marginatus	11	9	18	10	16
Constructipollenites ineffectus	-	2	-	2	-
Monoporites annulatus	3	-	2	2	6
Spinizonocolpites echinatus	-	-	-	-	-
Monocolpites marginatus	-	3	2	4	-
Mauritidiites crassibaculatus	1	-	-	1	-
Proxapertites cursus	-	-	-	-	-
Proteacidites segali	-	2	-	1	-
Psiltricolporites crassus	2	-	-	-	-
Psilatricolporites operculatus	-	2	-	2	-
Echiperiporites icacinoides	-	1	-	-	-
Auriculidites reticulatus	-	-	2	-	-
Longapertites vaneedenburgi	-	-	-	-	-
MARINE SPECIES					
Andalusiella polymorpha	-	2	2	-	-
Ceratiopsis diebeli	2	-	-	2	-
Senegaliniun sp.	1	1	-	-	-
Fibrocysta sp.	-	-	-	-	-
Phelodinium sp.	2	1	-	-	-
Cordosphaeridium sp.	-	-	-	-	-
Paleocystodinium austrialinium	1	2	2	-	-
Dinogymnium acuminatum	2	2	4	2	-
Spiniferites sp.	-	-	-	-	-
Oligosphaeridium complex	-	-	-	2	-
Andalusiella manthei	1	-	-	1	-
Cyclonephelium sp.	-	-	-	-	2
Achomosphaera sp.	-	-	-	2	6

Table 4.15d: The occurrence and distribution of palynomorphs species in the examined samples

Sample No. Palynomorphs species	ENU/20/001	ENU/21/003	ENU/22/001	ENU/23/001	ENU/24/001	ENU/25/001	ENU/27/001
TERRESTRIAL SPECIES							
Spores							
Foveotriletes margaritae	-	-	-	-	-	-	-
Laevigatosporites ovatus	21	11	26	9	13	8	10
Cyathidites minor	4	4	6	2	-	2	-
Cyathidites austrialis	-	-	-	2	4	-	-
Leiotriletes adriennis	2	-	2	-	-	4	-
Verrucatosporites usmensis	-	-	-	-	-	-	2
Cingulatisporites ornatus	1	1	2	-	2	-	-
Distaverrusporites simplex	-	-	-	1	-	1	2
Leiotriletes minor	2	-	1	4	4	1	-
Azolla marsulae	-	-	-	-	-	-	-
Matonisporites equiexinus	-	-	-	-	-	-	-
Pollen							
Buttinia andreevi	-	-	-	1	-	2	-
Proxapertites operculatus	-	-	-	-	1	2	-
Echitriporites trianguliformis	2	3	2	2	-	2	-
Retidiporites magdalenensis	-	-	-	2	1	-	-
Spinizonocolpites baculatus	-	-	-	-	-	-	-
Longapertites microfoveolatus	1	2	2	-	-	-	-
Longapertites marginatus	6	5	-	4	6	5	2
Constructipollenites ineffectus	2	-	1	-	-	-	-
Monoporites annulatus	-	4	2	2	-	3	-
Spinizonocolpites echinatus	1	-	-	1	-	-	1
Monocolpites marginatus	-	2	3	-	4	1	-
Mauritidiites crassibaculatus	-	-	-	-	1	-	-
Proxapertites cursus	-	-	-	-	-	1	-
Proteacidites segali.	2	-	-	1	2	-	-
Psiltricolporites crassus	-	1	-	2	-	-	2
Psilatricolporites operculatus	-	-	2	-	2	-	-
Echiperiporites icacinoides	-	-	-	-	-	-	-
Auriculidites reticulatus	-	-	-	-	-	-	-
Longapertites vaneedenburgi	2	-	4	-	-	-	-
MARINE SPECIES							
Andalusiella polymorpha	1	1	2	-	-	1	-
Ceratiopsis diebeli	-	-	-	-	2	-	-
Senegaliniun sp.	-	-	-	1	1	2	-
Fibrocysta sp.	-	-	-	-	-	-	-
Phelodinium sp.	-	-	-	-	-	-	-
Cordosphaeridium sp.	-	2	-	-	-	2	-
Paleocystodinium austrialinium	2	1	3	2	-	3	-
Dinogymnium acuminatum	2	2	4	2	1	4	-
Spiniferites sp.	-	1	-	-	3	-	-
Oligosphaeridium complex	-	-	2	-	-	1	-
Andalusiella manthei	1	-	-	3	2	-	-
Cyclonephelium sp.	-	-	-	-	-	-	-
Achomosphaera sp.	-	-	1	-	1	-	-

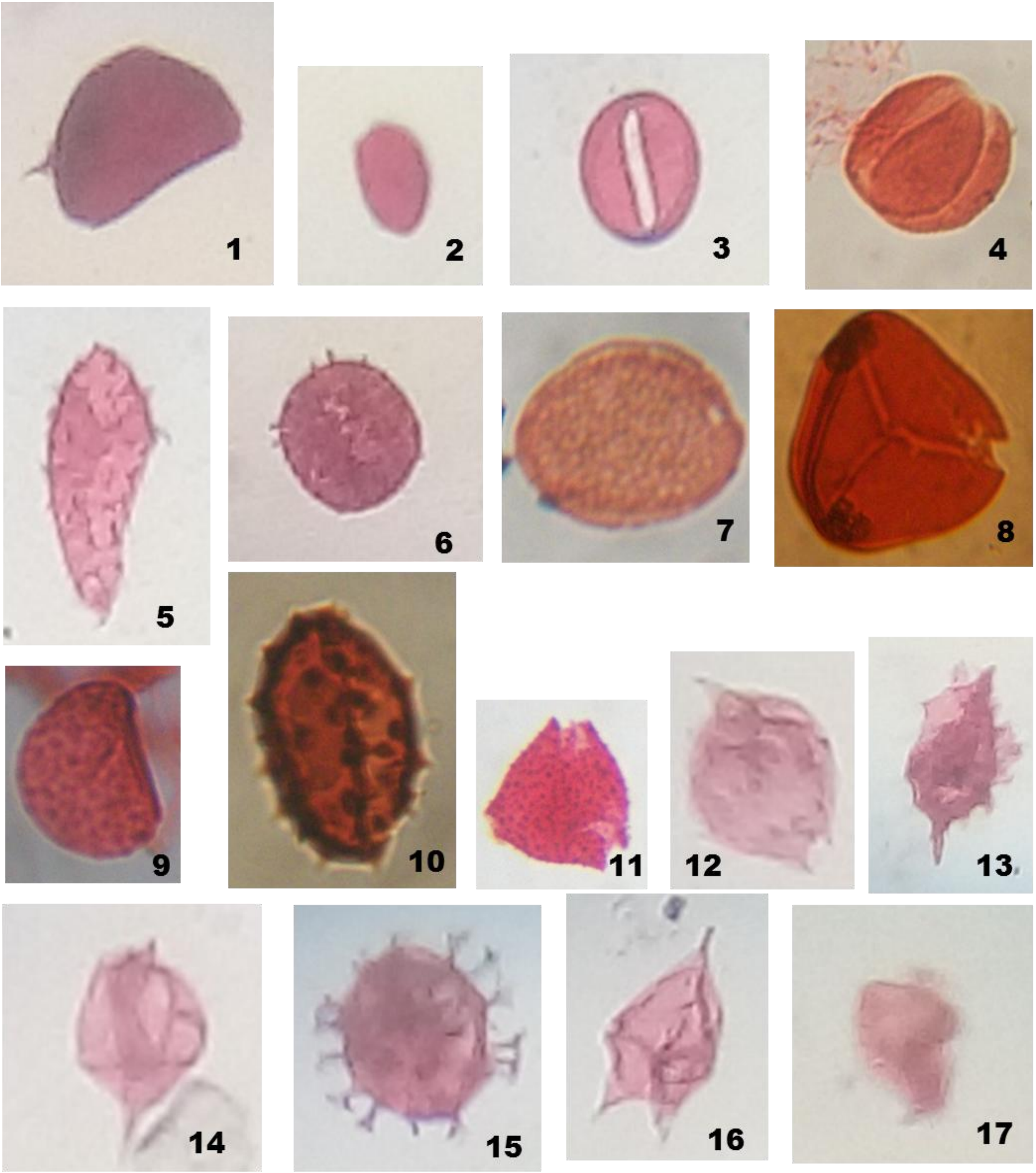

Fig. 4.54: Micrographs of some palynomorphs species recovered from the examined samples.

Magnifications nos. 4 and 8 (X 100 oil immersion), others (X 40)

Table 4.16: Micrograph names of some palynomorph species recovered in the examined samples.

S/N	Palynomorh Species
1	*Longapertites marginatus*
2	*Retidiporites magdalensis*
3	*Monocolpites marginatus*
4	*Proxapertites operculatus*
5	*Mauritidiites crassibaculatus*
6	*Spinizonocolpites baculatus*
7	*Proxapertites cursus*
8	*Cyathidites austrialis*
9	*Verrucatosporites usmensis*
10	*Spinizonocolpites echinatus*
11	*Echitroporites trianguliformis*
12	*Andalusiella manthei*
13	*Fibrocysta* sp.
14	*Andalusiella polymorpha*
15	*Olygosphaeridium complex*
16	*Ceratiopsis diebeli*
17	*Dinogymnium* sp.

Table 4.17a: The Average % of the palynomorphs speciesand their paloenvironments of deposistion of each examined sample of the Nkporo Formation

SAMPLE NO.	PALYNOMORPHS % FREQUENCY			PALEO-SALINITY	PALEOENVIRONMENTS OF DEPOSITION
	Spores	**Pollen**	**Marine Species**		
NKP/01/001	**30**	**44**	**26**	Brackish water	Marginal marine (Intermediate estuary)
NKP/03/002	**45**	**47**	**8**	Brackish water	Marginal marine (proximal estuary)
NKP/04/001	**40**	**45**	**15**	Brackish water	Marginal marine (proximal estuary)
NKP/LST/05/001	**37**	**37**	**26**	Brackish water	Shallow marine
NKP/06/001	**36**	**49**	**15**	Brackish water	Marginal marine (proximal estuary)
NKP/07/002	**19**	**21**	**60**	Brackish water	Distal estuary – open marine
NKP/08/001	**22**	**61**	**17**	Brackish water	Marginal marine (proximal estuary)
NKP/09/002	**13**	**25**	**62**	Brackish water	Distal estuary – open marine
NKP/10/001	**56**	**22**	**22**	Brackish water	Marginal marine (Intermediate estuary)
NKP/12/001	**29**	**30**	**41**	Brackish water	Marginal marine (distal estuary)
NKP/13/001	**39**	**29**	**32**	Brackish water	Marginal marine (distal estuary)
NKP/14/002	**42**	**42**	**16**	Brackish water	Marginal marine (proximal estuary)
NKP/15/001	**29**	**39**	**32**	Brackish water	Marginal marine (distal estuary)
NKP/16/002	**40**	**43**	**17**	Brackish water	Marginal marine (proximal estuary)
NKP/16/004	**40**	**45**	**15**	Brackish water	Marginal marine (proximal estuary)
NKP/16/008	**46**	**33**	**11**	Brackish water	Marginal marine (proximal estuary)
NKP/17/001	**33**	**50**	**17**	Brackish water	Marginal marine (proximal estuary)
NKP/17/003	**39**	**48**	**13**	Brackish water	Marginal marine (proximal estuary)
AVERAGE	**35.28**	**39.44**	**24.72**		

Table 4.17b: The Average % of the palynomorphs species and their paloenvironments of deposistion of each examined sample of the Enugu Shale

SAMPLE NO.	PALYNOMORPHS % FREQUENCY			PALEO-SALINITY	PALEOENVIRONMENTS OF DEPOSITION
	Spores	**Pollen**	**Marine Species**		
ENU/20/001	**58**	**31**	**11**	Brackish water	Marginal marine (proximal estuary)
ENU/21/003	**40**	**43**	**17**	Brackish water	Marginal marine (proximal estuary)
ENU/22/001	**57**	**25**	**18**	Brackish water	Marginal marine (proximal estuary)
ENU/23/001	**44**	**36**	**20**	Brackish water	Marginal marine (proximal estuary)
ENU/24/001	**46**	**34**	**20**	Brackish water	Marginal marine (proximal estuary)
ENU/25/001	**36**	**36**	**28**	Brackish water	Marginal marine (Intermediate estuary)
ENU/27/001	**74**	**26**	**0**	Fresh water	Mangrove swamp
AVERAGE	**50.71**	**33**	**16.29**		

The Nkporo Formation samples have average percent counts of spores of about 35.28%, pollens is 39.44% and marine species is about 24.72% (Table 4.17a). This is confirmed by the histogram plots showing the abundance of various classes of palynomorphs species of the Nkporo Formation samples (Figs 4.55a and 4.56a). The paleosalinity of the Nkporo Formation is brackish water. The environment of deposition is shallow marine.

The Enugu Shale samples have average percent counts of spores of about 50.71%, pollens is 33% and marine species is about 16.29% (Table 4.17a). This is confirmed by the histogram plots showing the abundance of various classes of palynomorphs species of the Nkporo Formation samples (Figs 4.55b and 4.56b). The paleosalinity of the Enugu Shale is mostly brackish water. The environment of deposition is marginal marine.

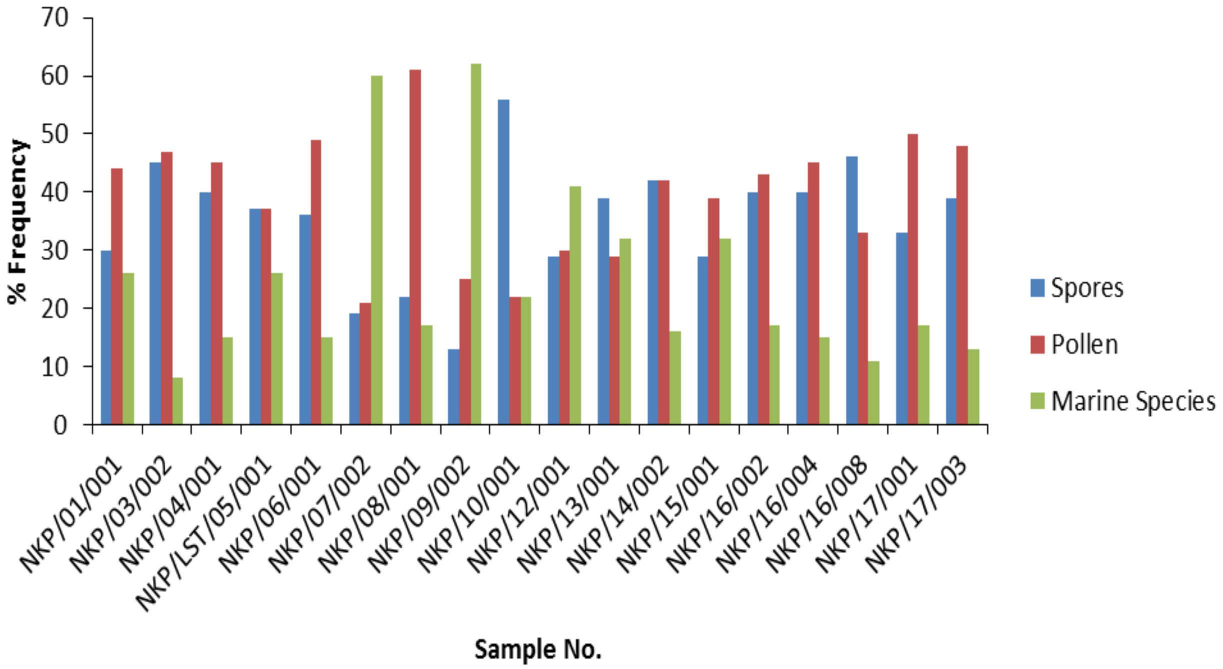

Fig. 4.55a: Histogram showing the % Frequency of Palynomorphs of the Nkporo Formation samples

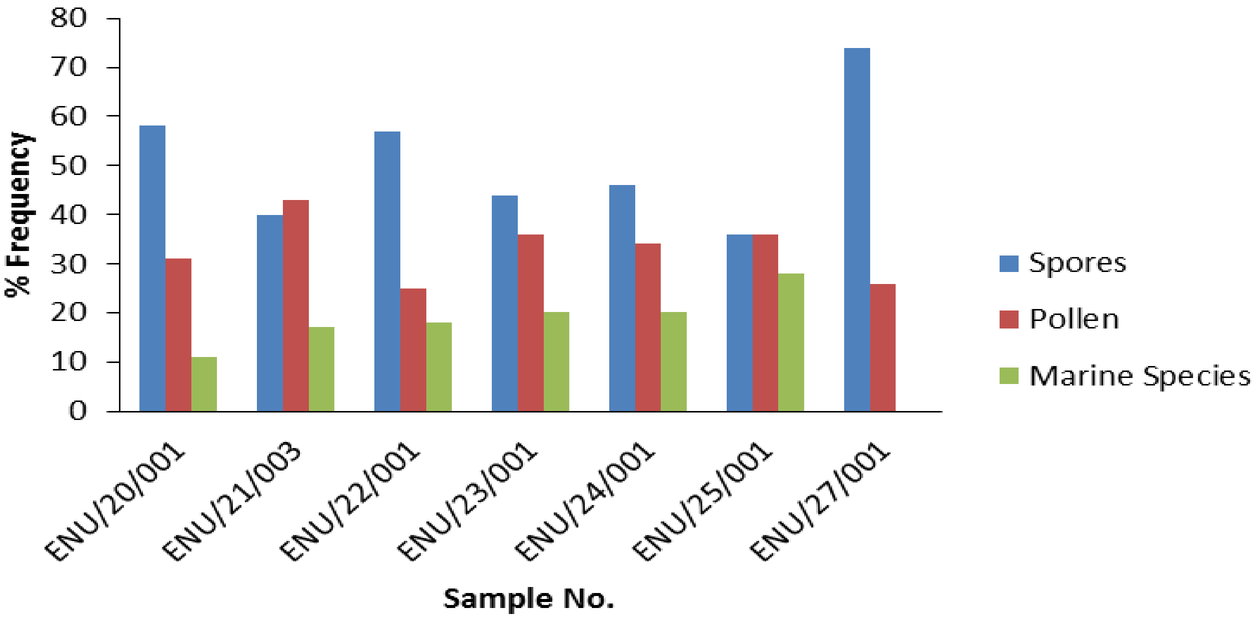

Fig. 4.55b: Histogram showing the % Frequency of Palynomorphs of the Enugu Shale samples

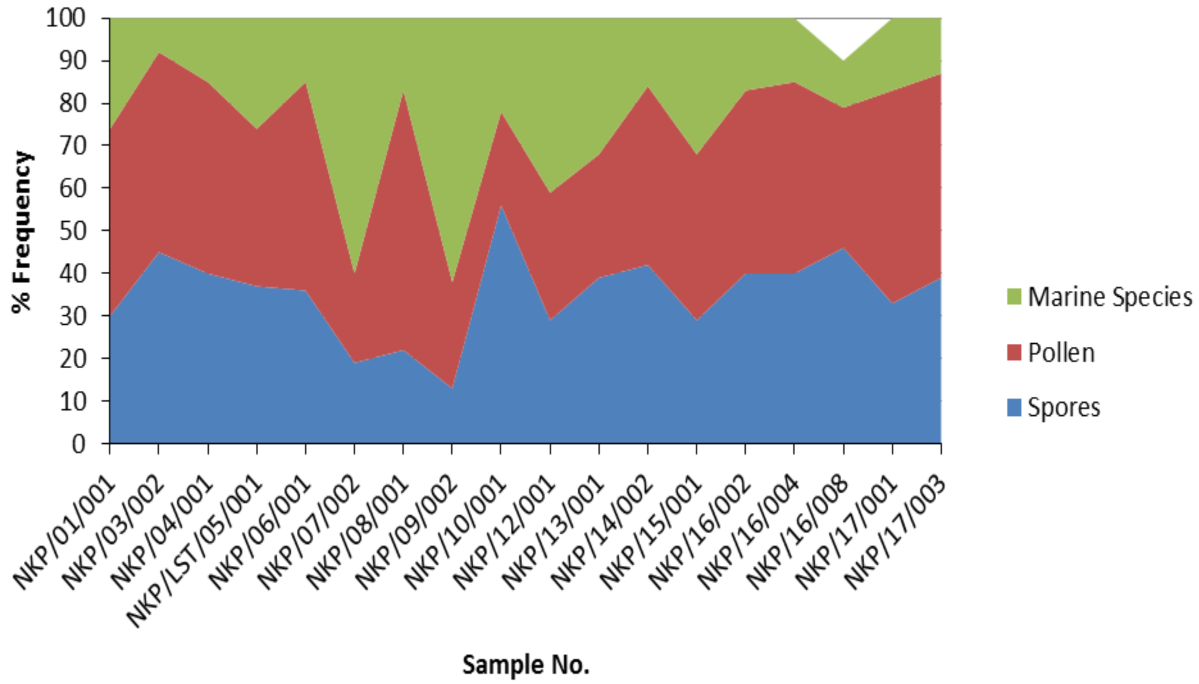

Fig. 4.56a: Area Chart showing the % Frequency of Palynomorphs of the Nkporo Formation samples

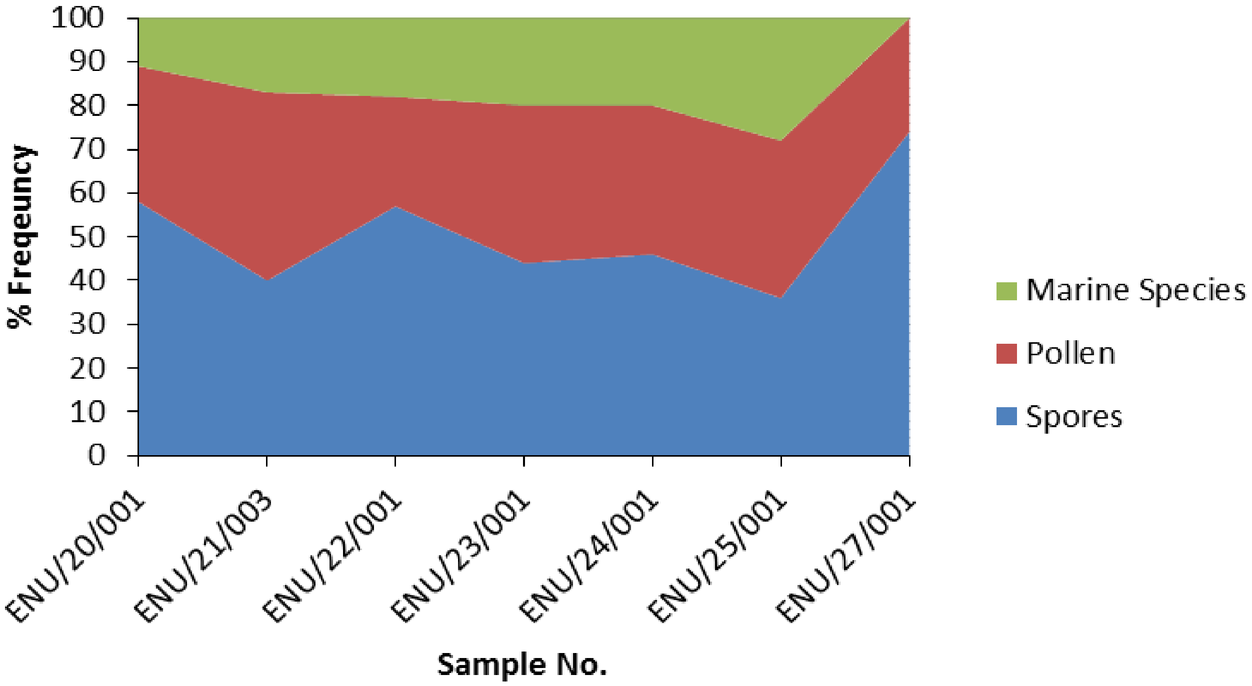

Fig. 4.56b: Area Chart showing the % Frequency of Palynomorphs of the Enugu Shale samples

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

This work was done to evaluate the source rocks and paleoenvironments of the Nkporo Formation and Enugu Shale (part of the Nkporo Group) in the Anambra Basin. The source rocks obtained from the twenty-five (25) shale samples were analyzed using a number of analytical procedures (geochemical analysis, and visual kerogen, biomarkers and palynological studies) in order to assess their hydrocarbon potentials and the age.

From the results of the geochemical analysis, The Total Organic Carbon (TOC) contents of the Nkporo Formation and Enugu Shale varied from 0.41 to 2.42wt.% and 0.53 to 3.15 wt.% respectively. This showed that Nkporo Formation and Enugu Shale had fair to very good organic matter contents. The organic matter richness varied from 0.08 to 4.40mgHC/g for the Nkporo Formation and 0.36 to 3.97mgHC/g for the Enugu Shale. Hydrogen Index versus Oxygen Index plots and visual kerogen showed that the Nkporo Formation was of Type III/IV while Enugu Shale was of Type II/III kerogen. The Thermal maturity index (Tmax) of the Nkporo Formation and Enugu Shale varied from 418 to 443°C and 430 to 443°C respectively. These suggested that the Nkporo Formation was marginally mature to mature while Enugu Shale was mature.

Visual Kerogen analysis was classified on the basis of Phytoclasts, Opaques, Amorphous Organic Matter (AOM) and Palynomorphs. The average percent counts of phytoclast is about 42.08%, that of Opaques is about 34.54%, Amorphous Organic Matter (AOM) is about 16.34% and Palynomorphs is about 7.08%. The highest number of percent counts produced is the phytoclast having the value of 42.08% which indicates Type III kerogen (Gas Prone) and Amorphous Organic Matter (AOM) having the value of 34.54% which indicate Oil/Gas Prone;

i.e from the results of the visual kerogen done for the Nkporo Group shows that the source rock is of Type III kerogen which is gas prone and also Type II/III which is Oil/Gas prone.

From the biomarker analysis, the distributions of *n*-alkanes showed that Nkporo and Enugu samples were formed from organic matter derived from both mixed organic sources and deposited in transitional environments. The isoprenoids (Pr/Ph) for the Nkporo Formation and Enugu Shale varied from 0.33 to 0.78 and 0.65 to 0.75 respectively; the two formations were therefore deposited in marine and marginal marine, reducing environments respectively. The presence of hopane, homohopane (C_{31}-C_{35}) in all the samples showed that bacteriohopanetetrol and other polyfunctional C_{35} hopanoids common in prokaryotic microorganisms have significant contributions to the organic matter. The occurrence of oleanene isomers in Nkporo Formation and Enugu Shale samples favoured marine organic matter deposited in lacustrine environment. In addition, the detection of gammacerane in Nkporo Formation and Enugu Shale samples represents marine water stratification during organic matter source deposition. The abundance of C_{29} Steranes and diasteranes in the samples indicate marine input of the organic matter.

From the palynological analysis, the age-diagnostic index palynomorphs such as *Dinogymnium* sp., *Andalusiella polymorpha, Andalusiella manthei, Senegalinium* sp., *Ceratiopsis diebeli*, and *Paleocystodinium austrialinium* were used to date the Nkporo Formation and Enugu Shale were within Late Campanian to Early Maastrichtian.

5.2 Conclusion

The evaluation of hydrocarbon potentials of the Nkporo Formation and Enugu Shale (part of the Nkporo Group) were undertaken. The Nkporo Formation is immature with fair to good Total Organic Carbon (TOC) content, Type III to IV kerogen and cannot generate hydrocarbon. The

Enugu Shale has a good to very good Total Organic Carbon (TOC) content with Type II/III (Oil/Gas Prone) kerogen and is mature to generate hydrocarbon.

The paleoenvironments of deposition for the Nkporo Formation was mostly anoxic, shallow marine while that of the Enugu Shale was anoxic, marginal marine environment. The age of the Nkporo Formation and Enugu Shale ranged from Late Campanian to Early Maastrichtian.

5.3 Recommendation

Due to the fact that the Enugu Shale is mature and can generate hydrocarbon, I strongly recommend that further studies should be done on that area (Enugu Shale) to know the migration pathways and accumulation of hydrocabon.

Contribution to Knowledge

This work has shown that the Enugu Shale has generated hydrocarbon contrary to the some views of previous authors said that it’s a potential of hydrocarbon. It is now certain that the Enugu Shale is mature and can generate hydrocarbon.

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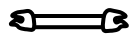
APPENDIX I

Symbols of Sedimentary Structures Modified (Nichols, 2005)

(1)		**Bivalves**
(2)		**Vertebrates**
(3)		**Plant materials**
(4)		**Gastropods**
(5)		**Mud cracks**
(6)		**Nodules and concretions**
(7)		**Biotubation**
(8)		**Wave ripple Cross- stratification**
(9)		**Planar Cross-bedding**